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UNIVERSITY OF ALBERTA

A MODEL STUDY OF THE $S_{RN}1$ POLYMERIZATION

BY

XICAI HUANG

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A THESIS
SUBMITTED TO THE FACULTY OF GRADUTE STUDIES
AND RESEARCH IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA
Fall, 1990

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ISBN 0-315-64773-6

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UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled

A MODEL STUDY OF THE $S_{RN}1$ POLYMERIZATION

submitted by XICAI HUANG in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

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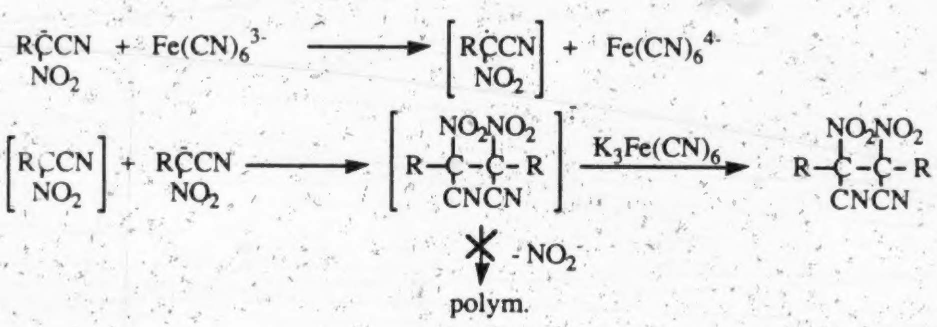
Abstract

Aliphatic substitution reactions by radical anion intermediates were discovered two decades ago. The reaction is useful for forming carbon-carbon bonds, especially for some highly substituted organic compounds because of the low steric sensitivity in radical reactions. It has been established that the reaction proceeds via a one-electron chain sequence in which a radical anion is produced in the initiation process. This can be illustrated in the following general equations, where R represents a wide variety of organic moieties, X is

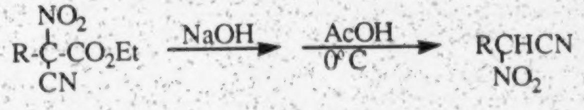
$$\begin{aligned} RX + e^- &\longrightarrow (RX)^{\overline{\cdot}} \\ (RX)^{\overline{\cdot}} &\longrightarrow R\cdot + X^- \\ R\cdot + A^- &\longrightarrow (RA)^{\overline{\cdot}} \\ (RA)^{\overline{\cdot}} + RX &\longrightarrow RA + (RX)^{\overline{\cdot}} \end{aligned}$$

a leaving group and A^- is an incoming nucleophile. The term $S_{RN}1$ is a simple symbolism to represent this sequence of reactions.

Since the $S_{RN}1$ reaction proceeds by a chain process, attempts were made to use the reaction for polymerization. We call this kind of polymerization a $S_{RN}1$ polymerization. Two kinds of $S_{RN}1$ polymerization

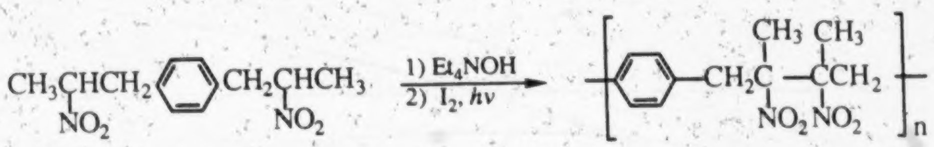


were attempted. The first kind was initiated by the reaction of the anion of 2-nitronitriles with $K_3Fe(CN)_6$. The dimer was produced when the anion of 2-nitronitriles reacted with excess $K_3Fe(CN)_6$ in aqueous solution, but no polymer was obtained. 2-Nitronitriles $RCH(NO_2)CN$ were isolated for the first time by treatment of 2-cyano-2-nitroesters with NaOH and subsequent acidification with acetic acid at 0°C.



$$\mathrm{R\text{-}}\overset{\mathrm{NO_2}}{\underset{\mathrm{CN}}{\mathrm{C}}}\mathrm{\text{-}CO_2Et} \xrightarrow{\mathrm{NaOH}} \xrightarrow[\mathrm{0^\circ C}]{\mathrm{AcOH}} \mathrm{R}\underset{\mathrm{NO_2}}{\mathrm{C}}\mathrm{HCN}$$

The second attempt was by treating compounds of a bifunctional electron donor with a bifunctional electron acceptor. The polymerization of 1,4-bis(2,2-dinitropropyl)benzene (acceptor) with the dilithium salt of 1,4-bis(2-nitropropyl)benzene (donor) was tried, but a polymer with average molecular weight 840 (trimer) was obtained. In order to know why the polymerization gave a trimer, the $S_{RN}1$ reaction of the model compound 2-nitro-1-phenylpropane was studied. From studies of the reaction of the model compound, four problems (disproportionation, solubility, ratio effect and reactivity) were discovered, which should influence the polymerization. These problems were solved by using tetraethylammonium nitronates and iodine for the coupling reaction. Thus, polymerization was induced using the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene with iodine to give a polymer with average molecular weight about 5000 after removal of nitro groups.



The Franchimont reaction, which is the dimerization resulting from the reaction of 2-bromoesters with NaCN, is discussed in the fifth chapter. The inhibition of the dimerization reaction of 2-bromoesters with cyanide ion was achieved by using a buffer or Et_4NCN. Attempts to inhibit the cyclization reaction of α,α'-dibromodiesters with cyanide ion using a buffer or Et_4NOH still remain to be investigated.

Acknowledgements

I wish to express my sincere appreciation and gratitude to Professor K.R. Kopecky for his outstanding guidance throughout the course of this research project. I am also grateful to him for his patience and many helpful suggestions during the preparation of this manuscript.

I am especially grateful to my wife not only for her support but also for her tremendous help in composing the diagrams for this thesis using the " Chem Draw" program for the Macintosh computer.

Finally, I would like to thank the University of Alberta for financial support.

Table of Contents

Page

I. Introduction... 1

II. Syntheses and attempted polymerization of 2-nitronitriles........ 27

  Synthesis... 28

  The decomposition mechanism of ethyl 2-cyano-2-nitrobutanoate.................................. 38

  Attempted polymerization of 2-nitronitriles.................... 42

III. The coupling reaction of the model compounds for the $S_{RN}1$ polymerization.. 48

  Synthesis and reactions of the model compound.............. 49

  Synthesis and reactions of 1,4-bis(2-nitropropyl)benzene... 71

  Other electron donors and acceptors.............................. 74

IV. Polymerization.. 82

V. Franchimont reaction.. 94

  The inhibition of the dimerization reaction of 2-bromoesters with NaCN.................................... 96

  The inhibition of the dimerization reaction of methyl α-bromophenylacetate with NaCN.................. 101

  The attempted synthesis of dimethyl 2,5-dicyanoadipate... 104

  The attempted synthesis of dimethyl 2,7-dicyanosuberate.. 109

VI. Experimental... 111

  Syntheses and reactions of 2-nitronitriles..................... 113

  Syntheses and reactions of model compounds................. 132

  Polymerization.. 161

  Franchimont reaction... 168

References... 178

List of Tables

Page

Table I. The yield of the dimer obtained in various solvents with different ratios of iodine and 2-nitro-1-phenylpropane..... 136

Table II. The yield of the dimer obtained with different solvents and reaction times.. 137

Table III. The yield of the dimer obtained in different solvents for the reaction of the lithium salt or the ammonium salt with the gem-dinitro compound 138

Table IV. Molecular weight of products obtained from different reaction conditions.. 162

Table V. Estimation of the concentration of Et_4NOH determined by the reaction of 2-nitro-1-phenylpropane with I_2 in various amounts of Et_4NOH 164

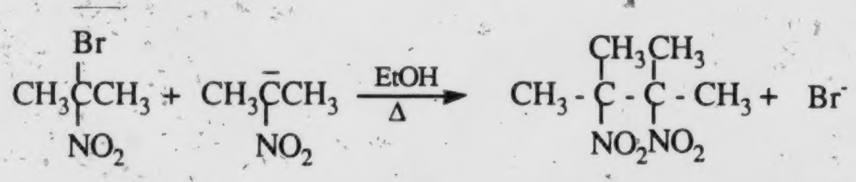
List of Figures

Page

Figure I. The structures of *cis* and *trans*
2,3-dimethyl-1,4-diphenyl-2-butene.............................. 69
Figure II. The structure of the anion 2-methyl-1-phenylallyl.......... 69
Figure III. The structures of *cis* and *trans*-
1,3-diphenyl-2-methylpropene.............................. 69

I. INTRODUCTION

Aliphatic substitution reactions involving radical anion intermediates were discovered two decades ago. The reaction is useful for forming carbon-carbon bonds, especially for some highly substituted organic compounds because of the low steric sensitivity in radical reactions.[1-5] The first reaction of this kind with α-halonitroalkanes was observed by Hass and Siegle[6] as early as 1940 (equation 1). However, it was not until 1966 that a reaction



$$CH_3\overset{\displaystyle Br}{\underset{\displaystyle NO_2}{C}}CH_3 + CH_3\underset{\displaystyle NO_2}{\bar{C}}CH_3 \xrightarrow[\Delta]{EtOH} CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}-\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}-CH_3 + Br^- \qquad (1)$$

mechanism was postulated by Kornblum[7] and Russell[8,9] and their co-workers for substitution at certain aliphatic sites, especially for reactions of nucleophiles with *p*-nitrobenzyl chloride or 2-chloro-2-nitropropane.

It has been established[4] that the reaction proceeds via a one-electron chain sequence in which a radical anion is produced in the initiation process. This can be illustrated in the following general equations 2-5, where R

$$RX + e^- \longrightarrow (RX)^{\cdot -} \qquad (2)$$

$$(RX)^{\cdot -} \longrightarrow R\cdot + X^- \qquad (3)$$

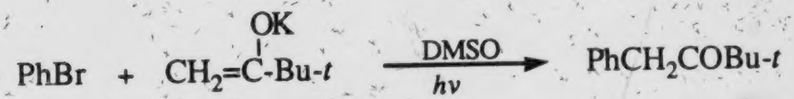
$$R\cdot + A^- \longrightarrow (RA)^{\cdot -} \qquad (4)$$

$$(RA)^{\cdot -} + RX \longrightarrow RA + (RX)^{\cdot -} \qquad (5)$$

represents a wide variety of organic moieties, X is a leaving group and A^- is an incoming nucleophile. The term $S_{RN}1$ standing for *substitution, radical nucleophilic, unimolecular,* was introduced by Bunnett[10] and is generally accepted for a simple symbolism to represent this sequence of reactions. This particular useful designation is used throughout this thesis.

There are two kinds of $S_{RN}1$ reactions depending on the types of the substrates. The first occurs with molecules in which the leaving group (X) is directly attached to a saturated carbon; this is usually referred to as an aliphatic $S_{RN}1$ reaction, although the substrate may contain certain unsaturated groups (e.g. *p*-nitrocumyl system). In the second type, the leaving group (X) is attached to an unsaturated, usually aromatic, carbon and is called an aromatic $S_{RN}1$ reaction, which was discovered in 1970 by Kim and Bunnett.[10]

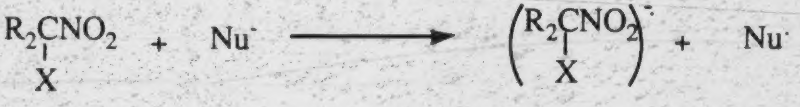
The conditions for these two types of $S_{RN}1$ reactions are quite different. For the aliphatic $S_{RN}1$ reaction, a weak nucleophile but good electron donor like the lithium salt of 2-nitropropane can be used for the substitution (e.g. equation 1), while for the aromatic $S_{RN}1$ reaction a strong nucleophile is especially favored as illustrated in equation 6.[11] Usually the reaction is carried out under photostimulation. In this case, the presence of a nitro group is not required, contrary to the substitution for the saturated system. The nitro group ever retards the aromatic $S_{RN}1$ process.[12] This thesis will mainly discuss the aliphatic $S_{RN}1$ reaction (or the saturated system).



$$PhBr + CH_2=\overset{\overset{\displaystyle OK}{|}}{C}\text{-}Bu\text{-}t \xrightarrow[h\nu]{DMSO} PhCH_2COBu\text{-}t \qquad (6)$$

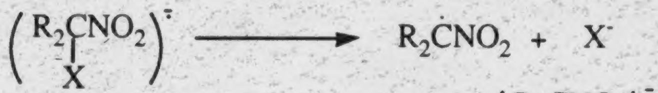
Although exceptions are known,[13] most aliphatic $S_{RN}1$ reactions require a nitro group either in the substrate or in the nucleophile to increase the reactivity. The nitro group is a good electron acceptor because of a low-energy π^* molecular orbital which allows the formation of a relatively stable radical anion. Therefore, reaction between a nitro compound and a nucleophile, which is able to act as an electron donor, will lead to an electron transfer as shown in equation 7. This step is usually called initiation. The dissociation of the radical anion forms a radical and an anion, which may be the rate determining step (equation 8 or 8'). The chain propagating process occurs in the next step by the combination of the radical with the nucleophile to form another radical anion (equation 9 or 9'). This radical anion will transfer the electron to $R_2C(X)NO_2$ (equation 10 or 10'). The termination step may involve coupling or disproportionation of two radicals (equation 11, 12 or 11', 12').

initiation

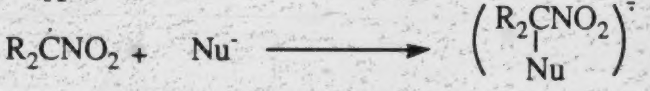


$$\underset{X}{R_2CNO_2} + Nu^- \longrightarrow \left(\underset{X}{R_2CNO_2}\right)^{\cdot -} + Nu^{\cdot} \qquad (7)$$

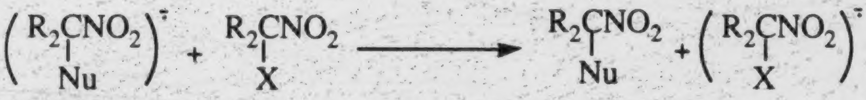
propagation path A



$$\left(\underset{X}{R_2CNO_2}\right)^{\cdot -} \longrightarrow R_2\dot{C}NO_2 + X^- \qquad (8)$$

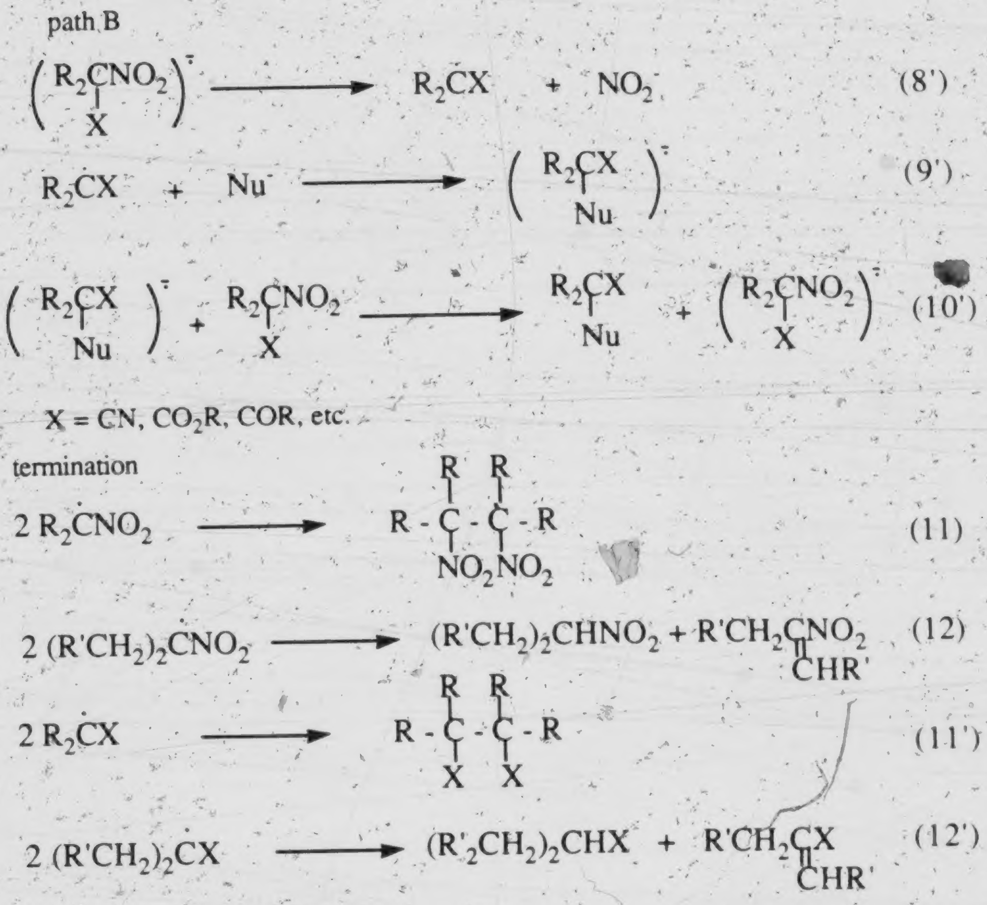


$$R_2\dot{C}NO_2 + Nu^- \longrightarrow \left(\underset{Nu}{R_2CNO_2}\right)^{\cdot -} \qquad (9)$$



$$\left(\underset{Nu}{R_2CNO_2}\right)^{\cdot -} + \underset{X}{R_2CNO_2} \longrightarrow \underset{Nu}{R_2CNO_2} + \left(\underset{X}{R_2CNO_2}\right)^{\cdot -} \qquad (10)$$

$X = NO_2, SO_2R$, I, Br, Cl, etc.

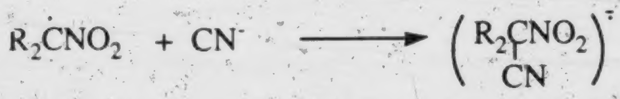

path B
(8')
(9')
(10')
X = CN, CO2R, COR, etc.
termination
(11)
(12)
(11')
(12')

Scheme 1. The $S_{RN}1$ reaction mechanism.

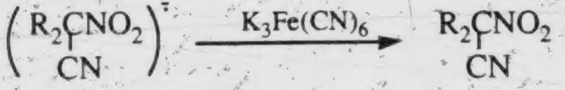
If X is a good leaving group (X = SO_2R, I, Br, Cl, etc.), the nitro group will remain during the reaction (path A). On the other hand, in the presence of a poor leaving group (X = CN, CO_2R, COR, etc.), breaking of the carbon-carbon bond is difficult and the substituion of the nitro group takes place (path B). Bowman has shown many other different leaving groups in a recent review.[1]

In most cases, the nucleophile in the $S_{RN}1$ reaction performs two functions. First, it may act as a single electron donor in the initiation step of the reaction. Secondly, it acts as a radical trap in the key propagating step in the $S_{RN}1$ reaction. In some cases, the reaction is initiated by some oxidizing reagents. For example, the reaction of nitronates $R_2CNO_2^-$ with sodium cyanide is initiated by potassium ferricyanide to give α-nitronitriles $R_2C(CN)NO_2$[14,15] (equation 13-15). In this case, cyanide ion only acts as an electron trap during the reaction, but the reaction is a non-chain process because there is no electron acceptor besides potassium ferricyanide. Although cyanide ion is a very good nucleophile, it is a relatively poor electron donor. There is only one report for the $S_{RN}1$ reaction when cyanide anion acts both as an electron donor and a radical trap; this happens in α-chloro-*p*-nitrocumene[16] (equation 16). The *p*-nitrocumyl system must be a very reactive substrate.

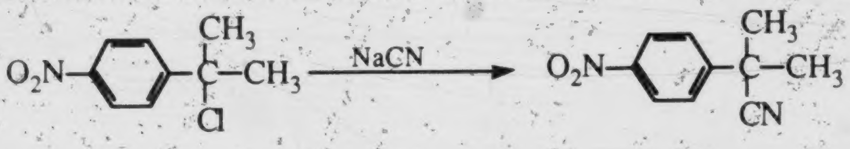
$$R_2\bar{C}NO_2 \xrightarrow{K_3Fe(CN)_6} R_2\dot{C}NO_2 \qquad (13)$$



$$R_2\dot{C}NO_2 + CN^- \longrightarrow \left(R_2\underset{CN}{C}NO_2\right)^{\dot{-}} \qquad (14)$$

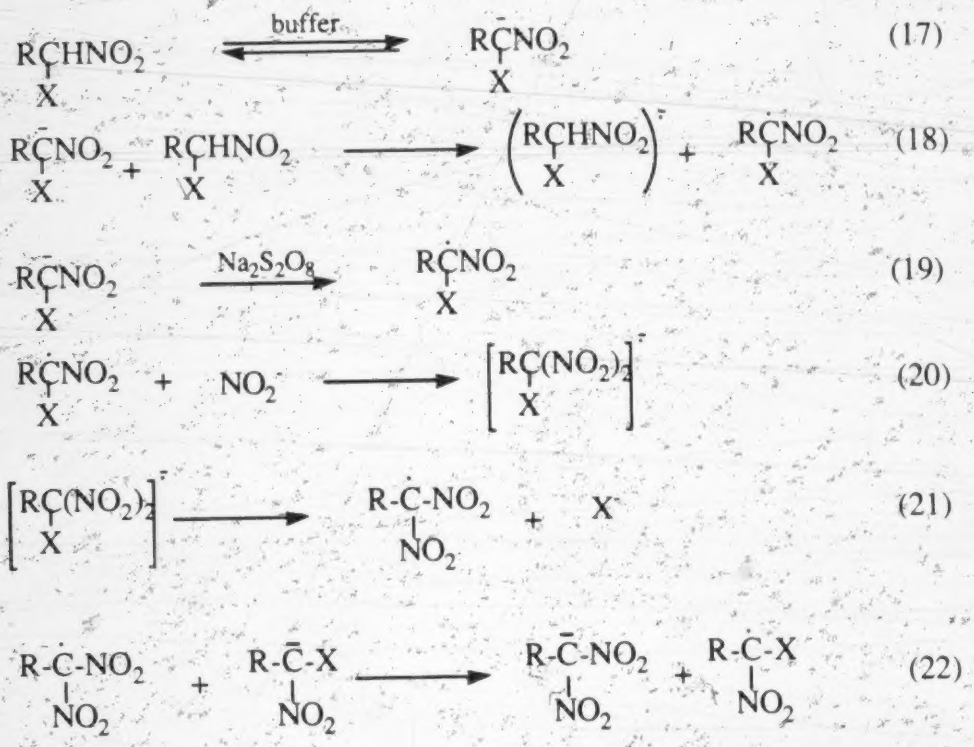


$$\left(R_2\underset{CN}{C}NO_2\right)^{\dot{-}} \xrightarrow{K_3Fe(CN)_6} R_2\underset{CN}{C}NO_2 \qquad (15)$$



(16)

The ter Meer reaction[17] is an another example of the reaction which can be initiated by an oxidizing reagent (Scheme 2). For example, the anions of 1-halo-1-nitroalkanes can react with sodium nitrite in the presence of sodium



Scheme 2. The ter Meer reaction mechanism.

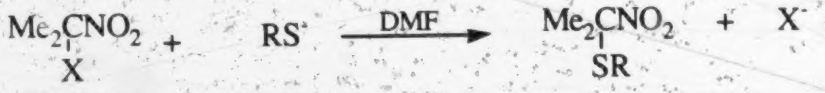
persulphate as an initiator (equation 19).[19,20] The reaction can also happen in moderately alkaline media without the oxidizing reagent. Therefore, 1-halo-1-nitroalkanes function as electron acceptors and the anions of 1-halo-1-nitroalkanes as electron donors (equation 18),[18] but the reaction in strong alkaline media does not take place because there is no neutral molecule as an electron acceptor. After the initiation, the nucleophile nitrite ion will combine with the radical to form the radical anion (equation 20). The resulting radical anion will lose a leaving group (a halide ion) to form a 1,1-dinitroalkyl radical (equation 21). The electron transfer from the anion of 1-halo-1-nitroalkane to the 1,1-dinitroalkyl radical permits the chain process to continue. Thus this is a chain reaction.

As mentioned by Kornblum,[2,4] the $S_{RN}1$ reaction is retarded by the presence of a strong electron acceptor like *p*-dinitrobenzene or radical traps such as oxygen and di-*t*-butylnitroxide because they will stop the chain reaction. The inhibition and light catalysis are the most common criteria for assigning the $S_{RN}1$ reaction. Inhibition studies have been discussed in detail.[8,9,16,21-23]

On the other hand, the $S_{RN}1$ reaction is highly accelerated in the presence of light. In certain reactions, light is absolutely required to stimulate the $S_{RN}1$ reaction for weakly basic nucleophiles.[24,25] In most $S_{RN}1$ reactions of $R_2C(X)NO_2$, neither the substrate nor the nucleophile absorb visible light, which suggests the presence of a charge transfer complex which is able to aborb light. The role of light catalysis is to energize the charge transfer complex between a substrate (acceptor) and a nucleophile (donor), hence enhancing the chance of electron transfer. Recent studies by Kornblum and co-workers clearly illustrate this principle.[16,20] The quantum yield was observed to be several hundred to 6000 for those reactions studied. The quantum yield is also wave length dependent, which also supports the proposal that the photochemical initiation proceeds preferentially via a charge transfer intermediate.

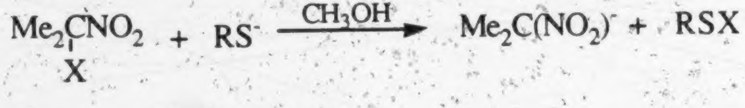
For the aromatic $S_{RN}1$ reactions, usually DMSO and liquid ammonia but not HMPA are the solvents of choice.[26] On the other hand, most $S_{RN}1$ reactions in saturated systems are carried out in dipolar aprotic solvents such as DMF, DMSO and HMPA because these solvents can increase both nucleophilicity and electron transfer capability in the order DMF < DMSO < HMPA.[2,4] Sometimes a reaction only takes place in HMPA but is slow in other solvents.[27] Solubility may be another factor because most of the nucleophiles are either inorganic compounds (e.g. $NaNO_2$) or lithium or sodium nitronates. However, when soluble salts like tetrabutylammonium nitronates are used, the reactions in other solvents like dichloromethane or benzene proceed even more rapidly than in dipolar aprotic solvents in the *p*-nitrobenzyl and *p*-nitrocumyl systems.[28,29]

Bowman has extensively studied the solvent effect on the $S_{RN}1$ reaction, especially for the nucleophiles like thiolates.[30-32] In dipolar aprotic solvents, the reactions between $Me_2C(X)NO_2$ and RS^- proceed largely by the $S_{RN}1$ mechanism (equation 23), but in methanol only disulphide products are



$$Me_2C(X)NO_2 + RS^- \xrightarrow{DMF} Me_2C(SR)NO_2 + X^- \qquad (23)$$

X = Cl, Br

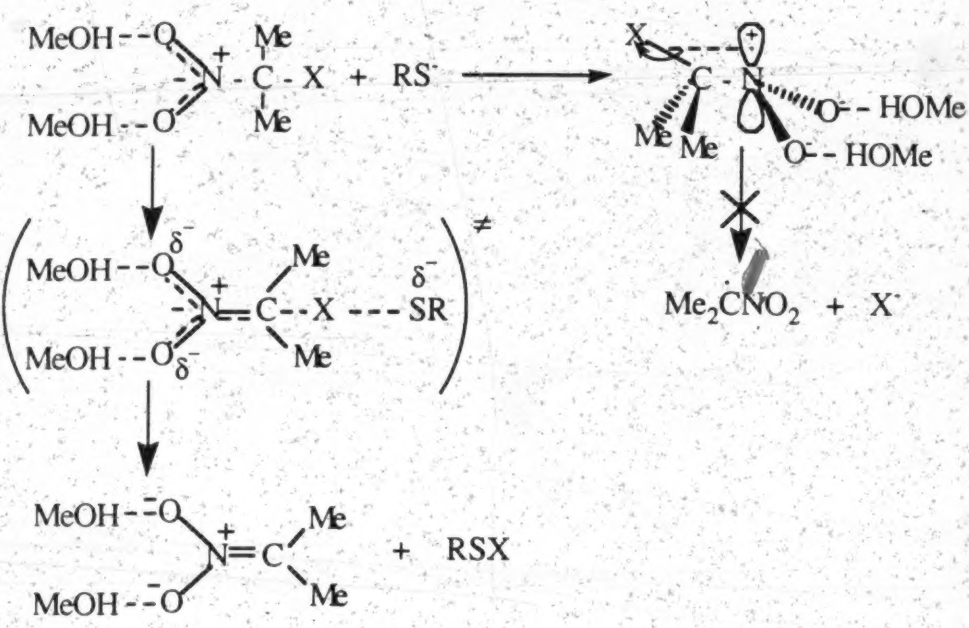


$$Me_2C(X)NO_2 + RS^- \xrightarrow{CH_3OH} Me_2C(NO_2)^- + RSX \qquad (24)$$

$$RSX + RS^- \longrightarrow RSSR \qquad (25)$$

obtained (equation 24 and 25). This is attributed to a solvation effect. Methanol can strongly solvate the intermediate radical anion in the $S_{RN}1$

mechanism, which retards its dissociation to the radical and the anion as shown in the Scheme 3, and hence retards the $S_{RN}1$ reaction. At the same

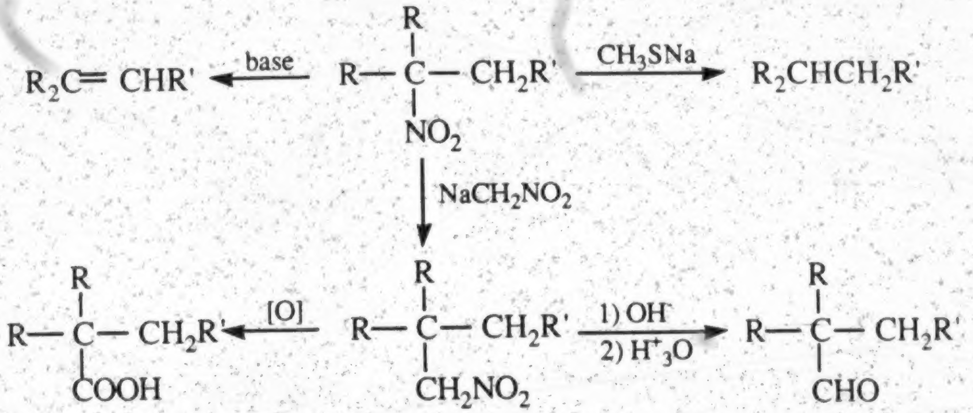


Scheme 3. Effect of MeOH solvation on the reaction between $Me_2C(X)NO_2$ and RS^-.

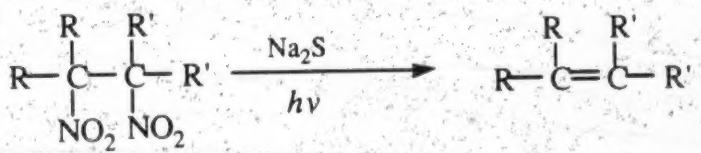
time, the increased solvation of $Me_2C(X)NO_2$ lowers the transition state energy of the S_N2 reaction on X, causing a faster competing reaction. Actually, this solvation effect can be observed in the reaction of the nitronates with NBS (N-bromosuccinimide) or NCS (N-chlorosuccinimide) in methanol. Only $R_2C(X)NO_2$ is obtained without further reaction of $R_2C(X)NO_2$ with $R_2CNO_2^-$ to form a dimer[33] (equation 26).

$$R_2\bar{C}NO_2 \xrightarrow[\text{or NCS / MeOH}]{\text{NBS / MeOH}} \underset{X = Cl, Br}{R_2C(X)NO_2} \qquad (26)$$

The $S_{RN}1$ reaction occurs readily under mild conditions and usually an excellent yield is obtained. In contrast to the S_N2 reaction, the reaction is rather insensitive to steric hindrance, which makes the reaction useful in constructing highly branched organic compounds. As shown in Scheme 4, if the nitro group in a product is not required after the reaction, it can be replaced by other groups such as hydrogen by selective reduction,[34] or nitromethylene by substitution with the anion of nitromethane. The nitromethylene group can be further converted to an aldehyde.[35] The nitro group can be also eliminated by a strong base to form alkenes.[36] In addition, vicinal nitro groups can be reduced to an alkene by the reaction with sodium sulfide (equation 27).[36] The



Scheme 4. Coversion of nitro groups into other functional groups.

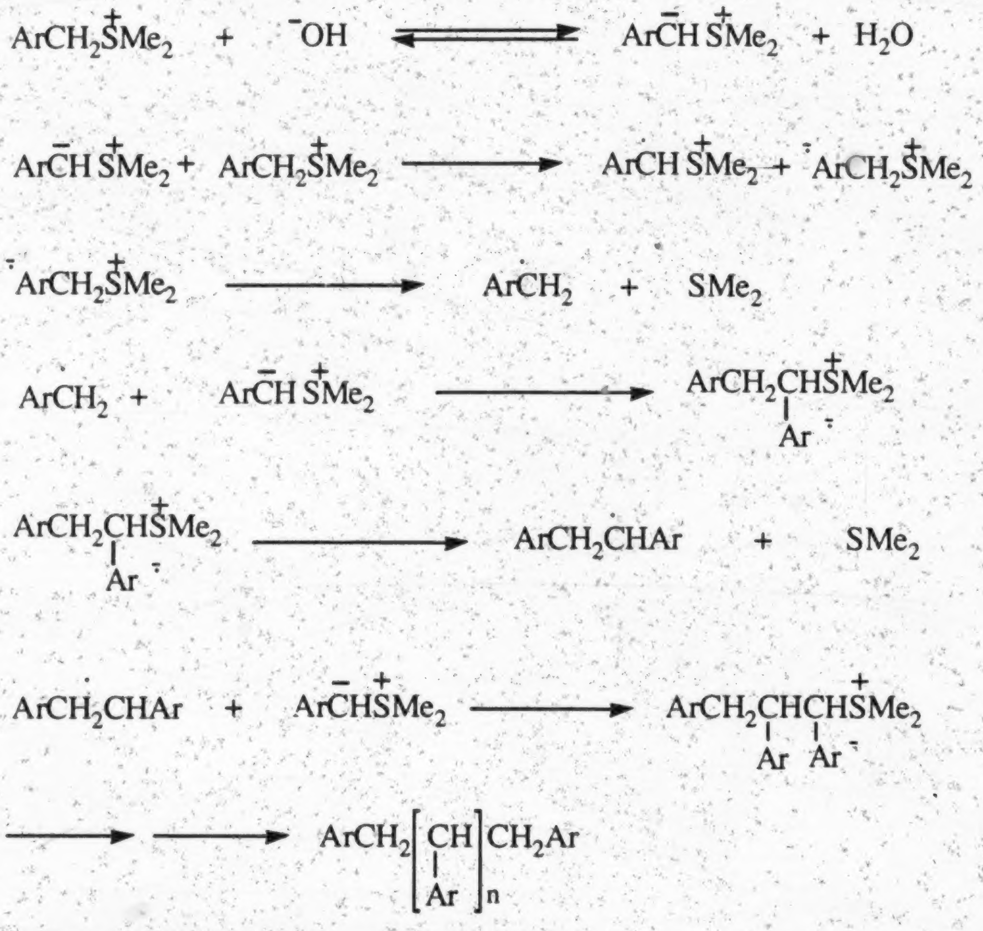


$$R-\overset{R}{\underset{NO_2}{C}}-\overset{R'}{\underset{NO_2}{C}}-R' \xrightarrow[h\nu]{Na_2S} R-\overset{R}{C}=\overset{R'}{C}-R' \qquad (27)$$

applications of the $S_{RN}1$ reaction in synthesis are quite unique because some compounds may be easily accessible only by this kind of reaction.

Applications for polymerization

Since the $S_{RN}1$ reaction is a chain process, we considered its possible application to polymerization. There should be three advantages: mild reaction



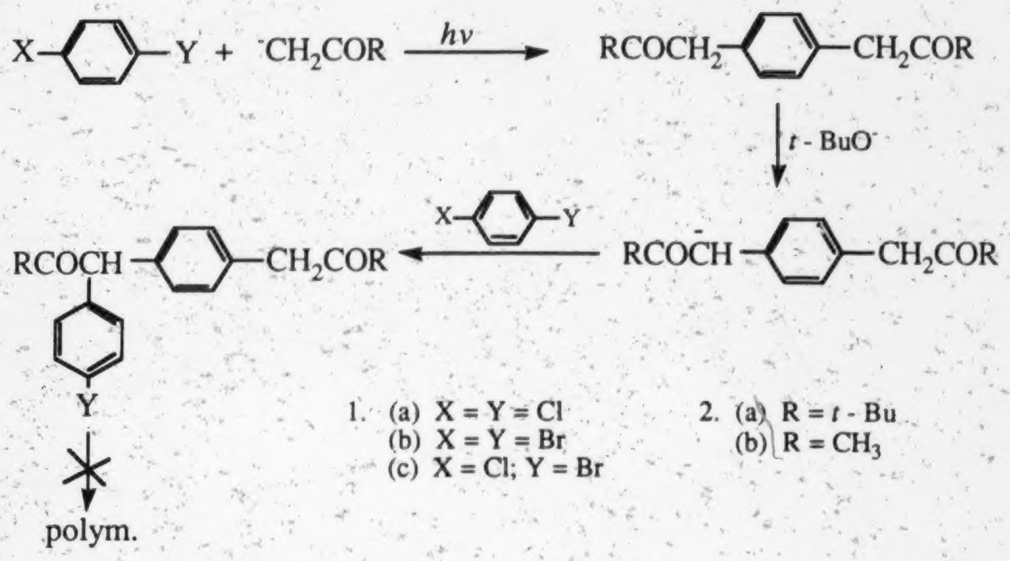
Scheme 5. Polymerization of *p*-nitrobenzyldimethylsulfonium tosylate.

conditions, low sensitivity to steric hindrance and most importantly unique polymer structure which may be impossible to obtain by other polymerization methods.

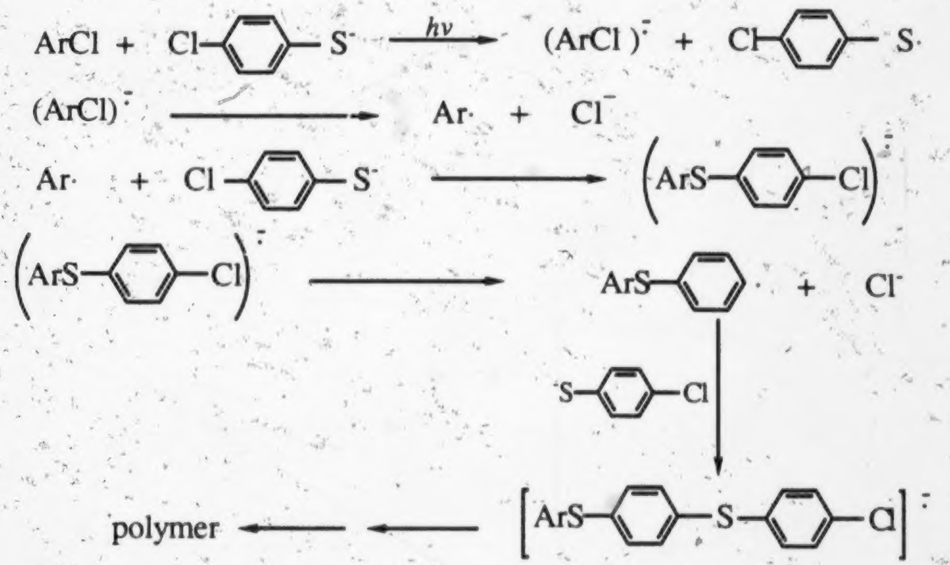
This kind of polymerization has been observed in the reaction of *p*-nitrobenzyldimethylsulfonium tosylate.[37,38] When the compound is treated with a base, it forms several dimeric products in 50% total yield. Another 50% is believed to be a polymer. The polymerization is illustrated in Scheme 5. The molecular weight is up to 1000, that is, the polymer chain is at least 8 units or longer. This reaction shows that the $S_{RN}1$ reaction could be used for the polymerization.

Alonso and Rossi have attempted to use the aromatic $S_{RN}1$ reaction for polymerization.[39] Two different approaches were used: (1) by the reaction of an aromatic substrate bearing two leaving groups and a nucleophile having more than one nucleophilic center; (2) by the reaction of a substrate having both the leaving group and the nucleophilic center within the same molecule.

The first attempt is illustrated in Scheme 6, but no polymerization was obtained. *p*-Dichlorobenzene can be substituted by ketone enolate ions under photostimulation, and thus the disubstituted product is produced. When the ketone is used in large excess, the chloride ion is eliminated in 83-93% yield, and a 65% yield of disubstituted product is obtained ($R = CMe_3$). However, when the photostimulated reaction of *p*-dichlorobenzene with the ketone and potassium *t*-butoxide is carried out in a ratio 1:1:4, the yield of chloride ion is only 25-50%. The low yield of chloride ion is attributed to two factors. The first one is due to the greatly reduced reactivity of the anion $^{-}C(Ar)HCOR$


hν
t - BuO⁻
polym.
1. (a) X = Y = Cl
(b) X = Y = Br
(c) X = Cl; Y = Br
2. (a) R = t - Bu
(b) R = CH3

Scheme 6. Attempted polymerization of p-XC_6H_4Y with $^{-}CH_2COR$.

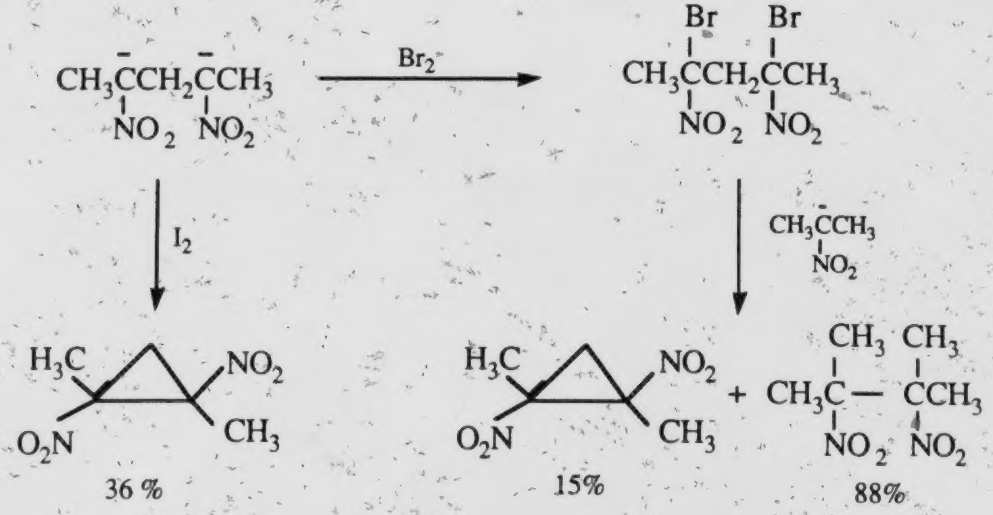


Scheme 7. Attempted polymerization of sodium p-chlorothiophenoxide.

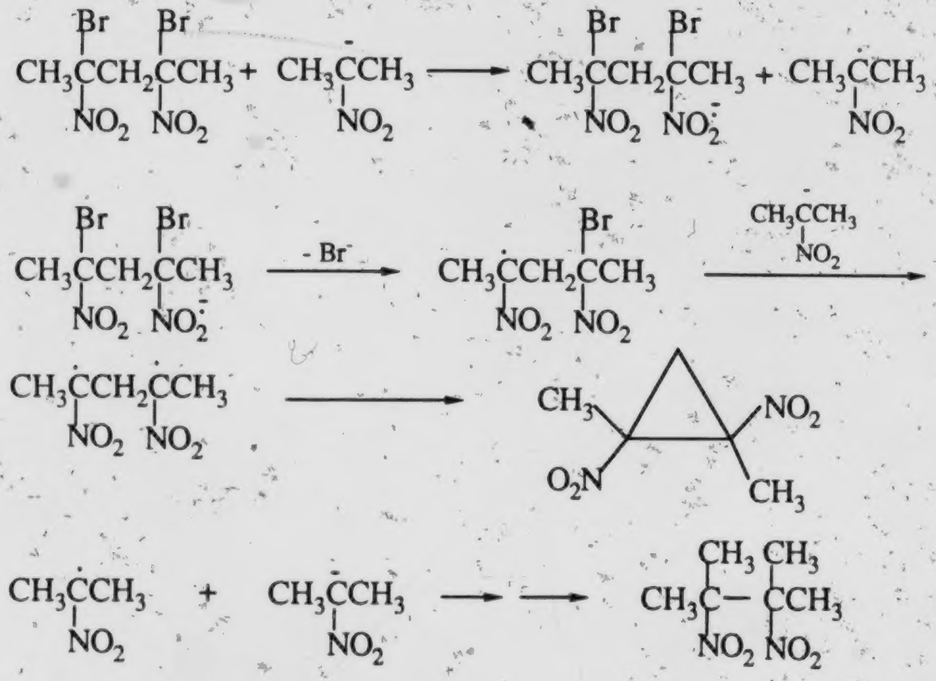
because of the complete conjugation with benzene ring. The second one results from the darkening of the solution during the reaction. It is clear at the beginning, but later becomes dark green and some solids form. Thus the reaction will be slowed down gradually because the possible light stimulation is greatly reduced by the darkening of the solution.

The second attempt is a system like sodium *p*-chlorothiophenoxide, which is illustrated in Scheme 7, but still no polymer was obtained. When a solution of *p*-chlorothiophenoxide ion is irradiated in liquid ammonia, some yellow solids form, but only a 20-23% yield of chloride ion can be detected. When they tried to increase the reactivity by entrainment with addition of more reactive substrates like chlorobenzene or 1-chloronaphthalene,[40] there was no increase in the yield of products. They suggested that the low yield of chloride ion for the reaction is caused by slow electron transfer initiation and low reactivity in the propagating steps. The suggestions were confirmed from model reactions.

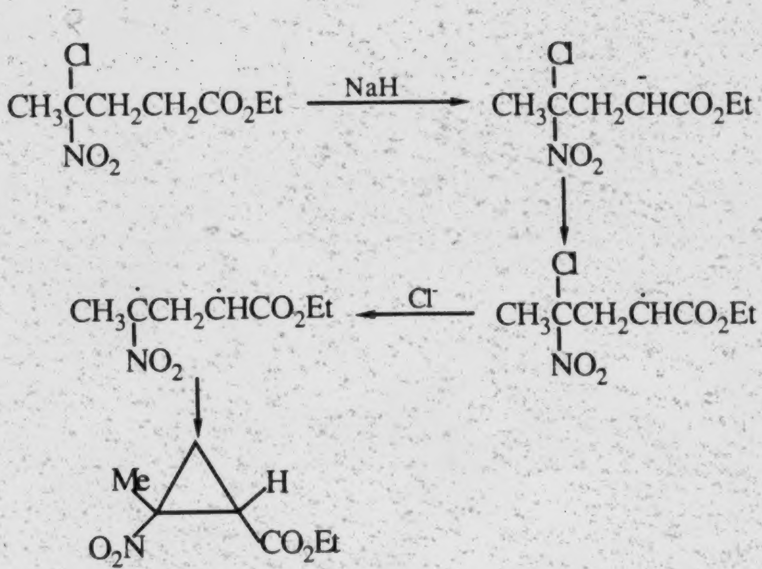
There are several interesting cyclizations to give a cyclopropane ring which result from $S_{ET}i$ (*substitution, electron transfer, intramolecular*) or S_Ni (*substitution, nucleophilic, intromolecular*) reactions.[41-45] In the case of 2,4-dibromo-2,4-dinitropentane, the reaction with the lithium salt of 2-nitropropane gives a cyclized product cyclopropane (Scheme 8), but no expected substitution product is obtained. The cyclopropane is produced by radical coupling as shown in Scheme 9. The cyclopropane can be also obtained in 36% yield by the reaction of the corresponding dianion with iodine. Also the reaction of ethyl 4-chloro-4-nitrovalerate with sodium



Scheme 8. Cyclization of the dianion of 2,4-dinitropentane.



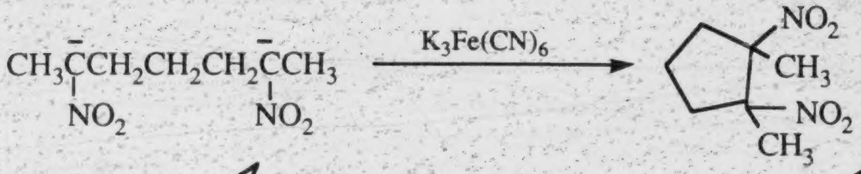
Scheme 9. Reaction mechanism of 2,4-dibromo-2,4-dinitropentane with the lithium salt of 2-nitropropane.



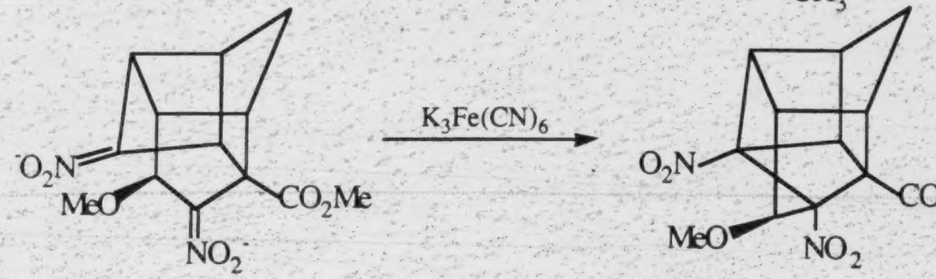
Scheme 10. Reaction of 4-chloro-4-nitrovalerate with NaH.

hydride (Scheme 10) only forms cyclization product. The reaction is believed to proceed by S_Ni mechanism, but the possible $S_{ET}i$ processes could not be excluded.[43] The cyclization reaction is the reason why no polymerization occurs. These compounds cannot be used for the $S_{RN}1$ polymerization.

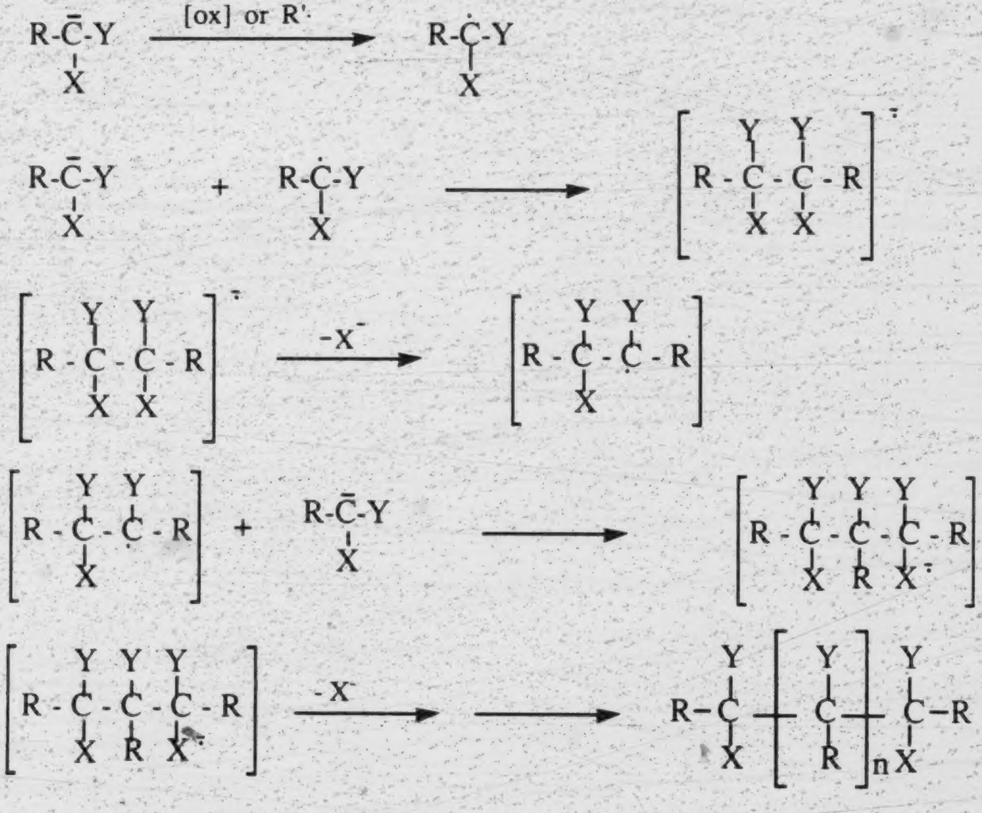
Based on the above examples, it can be expected that other bifunctional compounds will also cyclize to form four, five or six-membered rings. Bowman and Jackson have shown that the dianion of 2,6-dinitroheptane can be oxidized by potassium ferricyanide to 1,2-dinitro-1,2-dimethylcyclopentane in aqueous solution (equation 28).[46] No polymerization was observed because the cyclization to a small ring is fast and favored. The oxidizing cyclization to a four membered ring is shown in equation 29.[47] It should be expected that a longer chain dianion such as that of 2,8-dinitrononane may polymerize by iodine coupling because cyclization to a seven membered ring is slow.


CH₃C̄CH₂CH₂CH₂C̄CH₃
NO₂
NO₂
K₃Fe(CN)₆
NO₂
CH₃
NO₂
CH₃

(28)


⁻O₂N
MeO
NO₂⁻
CO₂Me
K₃Fe(CN)₆
O₂N
MeO
NO₂
CO₂Me

(29)

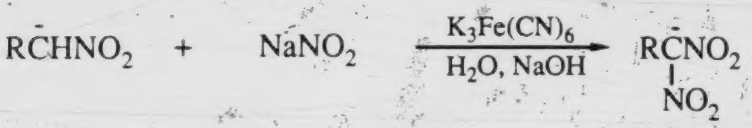

[ox] or R'·
-X⁻
-X⁻
R
X
Y
C
n

Scheme 11. The $S_{RN}1$ polymerization of $RC(X)Y^-$.

We considered two types of compounds for polymerization: (1) a compound bearing a leaving group and an electron withdrawing group at the same carbon; (2) a compound containing two secondary nitro groups and a rigid group or a long chain Z inside the molecule $RCH(NO_2)ZCH(NO_2)R$ to prevent cyclization.

(1). For the compounds of type one, the polymerization will follow the sequence shown in Scheme 11. Here, X is a leaving group and Y an electron acceptor. After the initiation by certain oxidizing reagents or radicals, the resulting radical will combine with $RC(X)Y^-$ to form a radical anion of the dimer. The radical anion may lose a leaving group X^- to form another radical. Thus the combination of the radical with $RC(X)Y^-$ permits the chain to grow and the polymerization may proceed in this way. For the compound RCH(X)Y to polymerize, the first thing that it should have is an acidic proton, so it can be easily converted to the anion by a base. The anion should have an ability to accept the radical after initiation. Thus, the polymerization can only take place at a primary carbon or a secondary carbon, but there are only a few examples for the $S_{RN}1$ reaction which take place at the primary carbon such as the anion of nitromethane.[35] As shown earlier, when there is a cyano group at the α-carbon, the nitro-group will be a leaving group during the $S_{RN}1$ reaction. The presence of a nitro group may be necessary to increase the reactivity for the reaction because nitro group is not only a good electron acceptor but also a good leaving group. Hence 2-nitronitriles should be the compounds ($X = NO_2$, $Y = CN$) to test our idea for the polymerization.

Because the polymerization occurs at a secondary carbon, we started to look for this kind of $S_{RN}1$ reaction. There are not many examples in the literature since most $S_{RN}1$ reactions take place at a tertiary carbon. The synthesis of 1,1-dinitroalkanes is one of the examples and is performed by the reaction of the anion of 1-nitroalkanes with sodium nitrite in the presence of potassium ferricyanide (equation 30). However, the method fails for the synthesis of secondary 2-nitronitriles (equation 31).[14] The ter Meer reaction is another interesting example (Scheme 2), which has been discussed earlier. However, 1-halo-1-nitroalkanes may not be suitable compounds for the polymerization because bromide or chloride ions may compete with the reaction initiated by sodium persulphate (equation 32).[48] Halide ions can react with sodium persulphate to form halogen atoms which can accept or destroy the radical anion and thus stop the chain reaction. In addition, the polymerization may not happen in aqueous solution because of solvation effects. The polymerization of 1,1-dinitroalkanes is impossible because the α-nitronitronates are oxidized to the corresponding acid by sodium persulphate

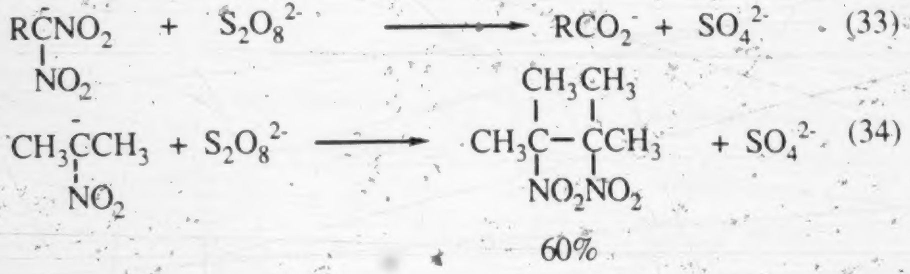


$$R\bar{C}HNO_2 \quad + \quad NaNO_2 \quad \xrightarrow[H_2O,\ NaOH]{K_3Fe(CN)_6} \quad R\bar{C}(NO_2)NO_2 \qquad (30)$$

$$R\bar{C}HNO_2 \quad + \quad NaCN \quad \xrightarrow[H_2O,\ NaOH]{K_3Fe(CN)_6} \quad \text{No reaction} \qquad (31)$$

$$2\,X^- \quad + \quad S_2O_8^{2-} \quad \longrightarrow \quad 2\,X\cdot \quad + \quad 2\,SO_4^{2-} \qquad (32)$$

in aqueous solution (equation 33).[49a] However, the reaction of the anion of 2-nitropropane with sodium persulphate gave the dimer in 60% yield (equation 34).[49] The anion of 2-nitropropane is a good electron donor and the oxidation potential may be low.

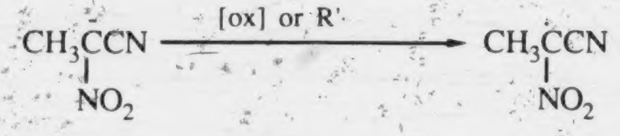


$$\underset{\displaystyle NO_2}{R\overset{-}{C}NO_2} + S_2O_8^{2-} \longrightarrow RCO_2^{-} + SO_4^{2-} \qquad (33)$$

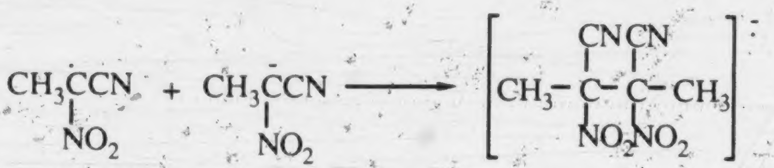
$$CH_3\underset{\displaystyle NO_2}{\overset{-}{C}}CH_3 + S_2O_8^{2-} \longrightarrow \underset{60\%}{CH_3\underset{\displaystyle NO_2}{\overset{\displaystyle CH_3}{C}}-\underset{\displaystyle NO_2}{\overset{\displaystyle CH_3}{C}}CH_3} + SO_4^{2-} \qquad (34)$$

The polymerization of 2-nitropropanenitrile should proceed as indicated in equations 35-38. The chain propagating step proceeds by the combination of the radical and the anion and is the most important step (equation 36). This radical anion may lose a nitro group to form the radical of the dimer (equation 37). The recombination of the radical and $RC(NO_2)CN^-$ forms the radical anion of the trimer (equation 38). The process will repeat to produce the polymer. The termination probably takes place by coupling or disproportionation of two radicals.

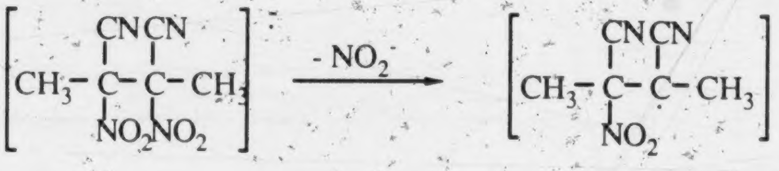
There is no available synthesis of 2-nitropropanenitrile and the chemical and physical properties of the compound are not known. Because of the solvation effect, it seems that the polymerization in aqueous solution is unlikely. If the oxidation potential of the anion of 2-nitropropanenitrile is high, a suitable initiator might be used in an aprotic solvent to initiate the polymerization.



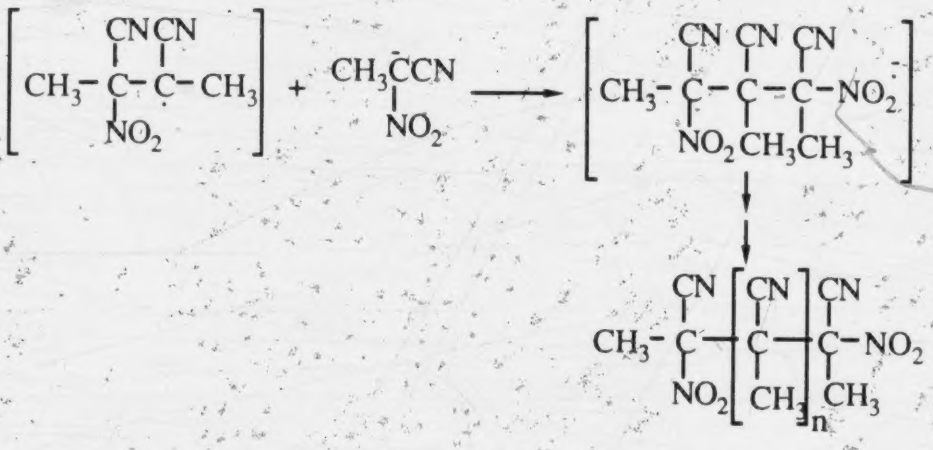
$$\underset{\mathrm{NO_2}}{\mathrm{CH_3\overset{-}{C}CN}} \xrightarrow{[\mathrm{ox}]\ \mathrm{or}\ \mathrm{R}^{\cdot}} \underset{\mathrm{NO_2}}{\mathrm{CH_3\dot{C}CN}} \qquad (35)$$



$$\underset{\mathrm{NO_2}}{\mathrm{CH_3\dot{C}CN}} + \underset{\mathrm{NO_2}}{\mathrm{CH_3\overset{-}{C}CN}} \longrightarrow \left[\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}-\underset{NO_2}{\overset{CN}{C}}-CH_3}\right]^{\dot{-}} \qquad (36)$$



$$\left[\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}-\underset{NO_2}{\overset{CN}{C}}-CH_3}\right]^{\dot{-}} \xrightarrow{-\ \mathrm{NO_2^-}} \left[\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}-\overset{CN}{\dot{C}}-CH_3}\right] \qquad (37)$$



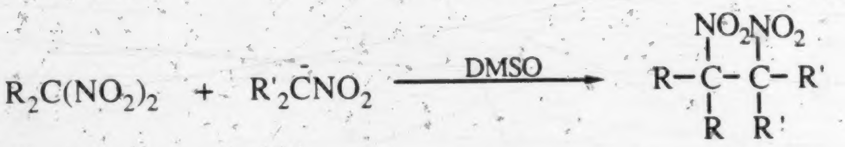
$$\left[\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}-\overset{CN}{\dot{C}}-CH_3}\right] + \underset{\mathrm{NO_2}}{\mathrm{CH_3\overset{-}{C}CN}} \longrightarrow \left[\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}-\underset{CH_3}{\overset{CN}{C}}-\underset{CH_3}{\overset{CN}{C}}-NO_2}\right]^{\dot{-}} \qquad (38)$$

$$\downarrow$$

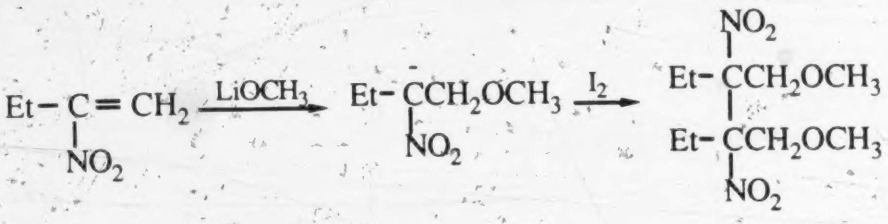
$$\mathrm{CH_3-\underset{NO_2}{\overset{CN}{C}}}\!\left[\mathrm{\underset{CH_3}{\overset{CN}{C}}}\right]_n\!\mathrm{\underset{CH_3}{\overset{CN}{C}}-NO_2}$$

(2). For the compound $RCH(NO_2)ZCH(NO_2)R$ to polymerize, Z should be rigid or a long chain so that the cyclization can be avoided. It seems that a benzene ring could meet the requirement. Since there is no available synthesis of 1,4-bis(1-nitroethyl)benzene ($Z = C_6H_4$), 1,4-bis(2-nitropropyl)benzene ($Z = CH_2C_6H_4CH_2$) was used instead to test the possibility of this kind of polymerization. The disubstituted compound can be made by using an available method for the preparation of the corresponding mono-substituted compound.

The coupling reaction conditions for forming a C-C bond have been extensively studied by Kornblum.[2,4] A usual coupling reaction is by *gem*-dinitro compounds with lithium nitronates (equation 39).[50] In the presence of



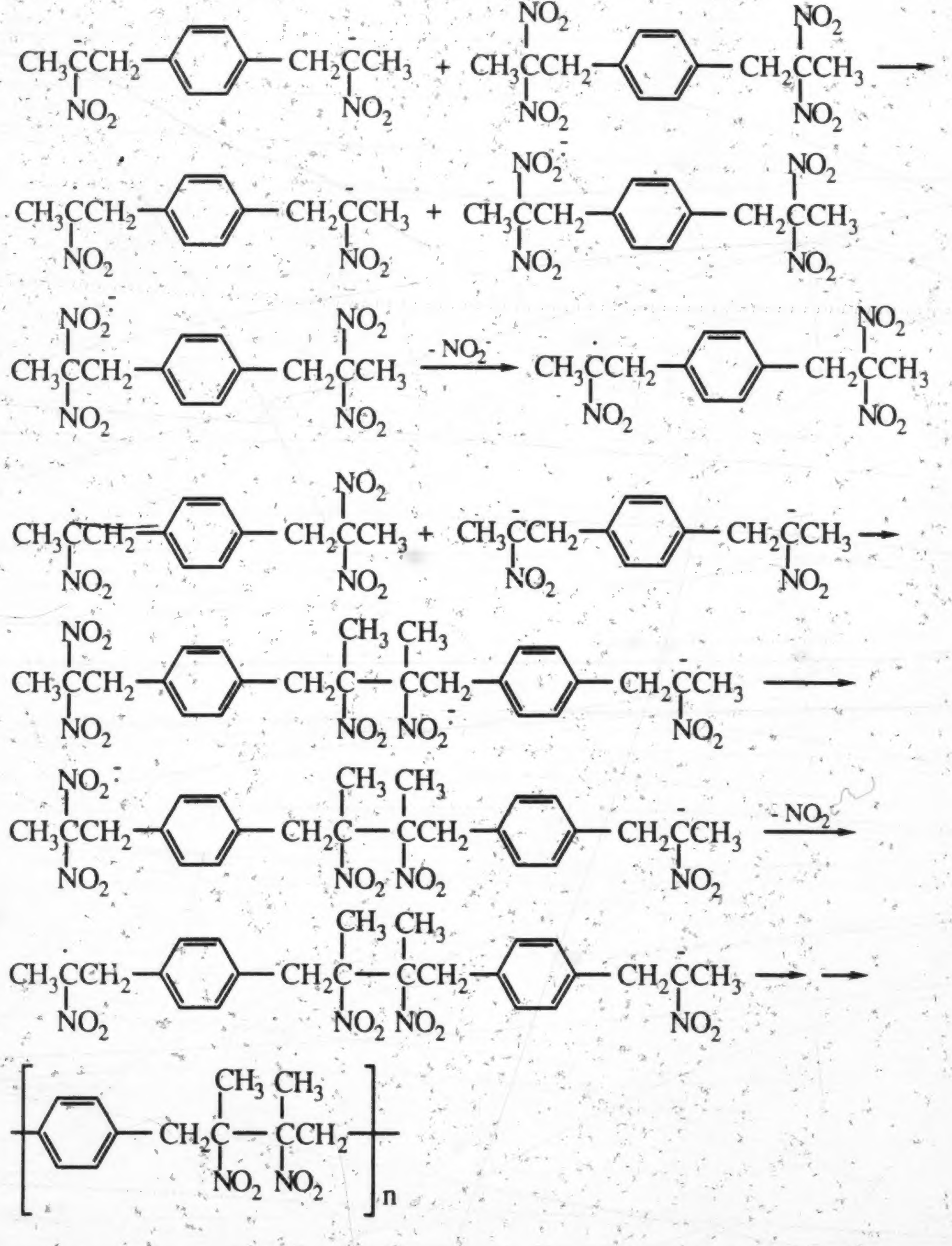
$$R_2C(NO_2)_2 + R'_2\overset{-}{C}NO_2 \xrightarrow{DMSO} R-\underset{R}{\overset{NO_2}{C}}-\underset{R'}{\overset{NO_2}{C}}-R' \qquad (39)$$



$$Et-\underset{NO_2}{C}=CH_2 \xrightarrow{LiOCH_3} Et-\underset{NO_2}{\overset{-}{C}}CH_2OCH_3 \xrightarrow{I_2} \begin{array}{c} NO_2 \\ | \\ Et-CCH_2OCH_3 \\ | \\ Et-CCH_2OCH_3 \\ | \\ NO_2 \end{array} \qquad (40)$$

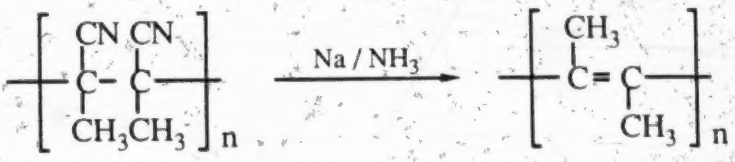
excess lithium salt (2 equivalents), the coupling reaction always gives an excellent yield. Another method was also mentioned by Kornblum and Cheng[51] by using iodine with lithium nitronates (equation 40). Illumination can increase the reaction rate. Therefore the polymerization might be accomplished by using 1,4-bis(2,2-dinitro-propyl)benzene as an acceptor and the dilithium salt of 1,4-bis(2-nitropropyl)benzene as a donor (Scheme 12). This unique polymer is only accessible by the $S_{RN}1$ reaction. Since the polymer contains so many nitro groups, it may be useful after further modification.

The polymer obtained from 2-nitropropanenitrile contains many vicinal cyano-groups, which can be reduced to double bonds[52] (equation 41). After



Scheme 12. polymerization of the dilithium salt of 1,4-bis(2-nitropropyl)benzene with 1,4-bis(2,2-dinitropropyl)benzene.

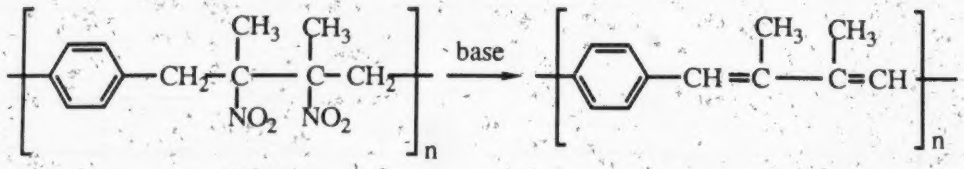
the reduction, the polymer has a structure of conjugated double bonds and so may be a useful conducting or semi-conducting material.



$$\left[-\overset{CN}{\underset{CH_3}{C}}-\overset{CN}{\underset{CH_3}{C}}- \right]_n \xrightarrow{Na / NH_3} \left[-\overset{CH_3}{C}=\underset{CH_3}{C}- \right]_n \qquad (41)$$

Conducting polymers are potentially useful materials although the real applications still remain under investigation. This kind of material has been extensively studied in recent years.[53-56] The most common systems are polyacetylene, polythiophene, polyphenylene and polyaniline. The major problem is the solubility of the polymer. Because of the conjugated double bonds, it is rigid, brittle and intractable. This largely limits the real application of the conducting polymer. The attempt to make a copolymer with styrene and to increase the solubility only decreases the conductivity. The introduction of a *t*-butyl group into thiophene make the polymer soluble.[57] The polymer was made by chemical polymerization instead of the usual electrochemical polymerization. The solubility allows molecular weights to be measured. About 200-300 thiophene units are detected and this polymer shows conductivity comparable to that of a semi-conductor. Although the polymer chain is still not quite long enough, this may be the way to solve the solubility problem of the conducting polymer.

The polymer that would be obtained from the second type of polymerization contains nitro groups that can be easily modified. If the nitro groups are removed by treating with a strong base, the polymer will have a



(42)

structure containing conjugated double bonds (equation 42). This is another kind of conducting polymer. It may be possible to introduce a big group into the benzene ring before polymerization to make the polymer soluble without decreasing the reactivity because the radical reaction has a low sensitivity to ring substitutents. This kind of polymerization may be the alternative way to make a soluble conducting polymer.

Since there was no available method for the synthesis of 2-nitronitriles, many efforts were made to prepare these compounds. A new method was developed and is useful for their synthesis. The synthesis and attempted polymerization of 2-nitronitriles will be discussed in the second chapter.

During studies of the polymerization of 1,4-bis(2-nitropropyl)benzene, we found several problems which lead to a low molecular weight polymer (trimer). By studying the reaction of the model compound, 2-nitro-1-phenylpropane, these problems were solved by using the tetraethylammonium salt for the polymerization. The reaction of the model compound will be discussed in the third chapter and the polymerization in the fourth chapter.

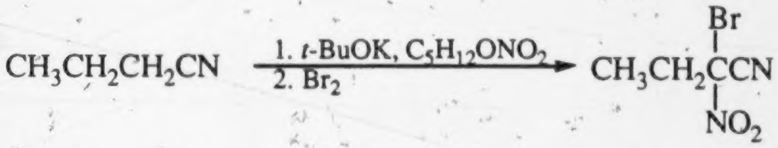
In the process of synthesis of 2-nitropropanenitrile, we discovered that the dimerization resulting from the reaction of 2-bromoesters with sodium cyanide can be inhibited by using a buffer or tetraethylammonium cyanide.

These methods were applied for the attempted synthesis of α,α'-dicyanodiesters, which will be discussed in the fifth chapter.

II. SYNTHESES AND ATTEMPTED POLYMERIZATION OF 2-NITRONITRILES

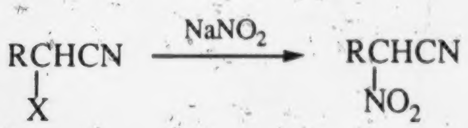
At the outset of this study, 2-nitropropanenitrile was an unknown compound. The homologous compounds, nitroacetonitrile and the potassium salt of 2-nitrobutanenitrile have been made by different methods. Nitroacetonitrile was made by the reaction of nitromethane with KOH followed by acidification and subsequent dehydration of the resulting methazonic acid [58,59] (equation 43). The potassium salt of 2-nitrobutanenitrile

$$CH_3NO_2 \xrightarrow[2.\ H_3O^+]{1.\ KOH} O_2NCH_2CHNOH \xrightarrow{SOCl_2} O_2NCH_2CN \quad (43)$$



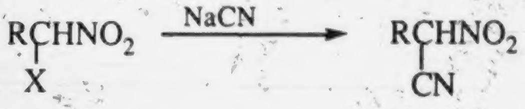
$$CH_3CH_2CH_2CN \xrightarrow[2.\ Br_2]{1.\ t\text{-}BuOK,\ C_5H_{12}ONO_2} CH_3CH_2\overset{\displaystyle Br}{\underset{\displaystyle NO_2}{C}}CN \quad (44)$$

was made in moderate yield by the reaction of 1-butanenitrile with amyl nitrate in the presence of potassium *t*-butoxide[60] (equation 44), but only its brominated product 2-bromo-2-nitrobutanenitrile was isolated. Thus, an alternative way was investigated for the synthesis of 2-nitropropanenitrile. We



$$R\underset{\displaystyle X}{C}HCN \xrightarrow{NaNO_2} R\underset{\displaystyle NO_2}{C}HCN \quad (45a)$$

X= OTs, I, etc.



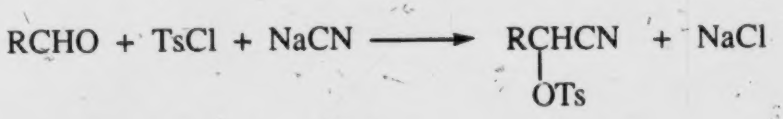
$$R\underset{\displaystyle X}{C}HNO_2 \xrightarrow{NaCN} R\underset{\displaystyle CN}{C}HNO_2 \quad (45b)$$

first tried to make 2-nitropropanenitrile by the reaction of the α-substituted propanenitriles $CH_3CH(X)CN$ with sodium nitrite (equation 45a). We also tried to make 2-nitropropanenitrile by the reaction of α-substituted nitroethanes $CH_3CH(X)NO_2$ with cyanide ion (equation 45b). Both attempts were unsuccessful. A five-step synthesis was thus developed to make 2-nitropropanenitrile in 66% total yield.

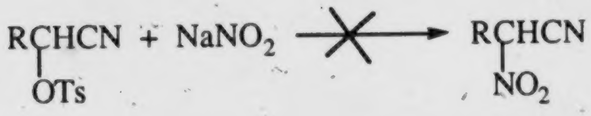
Results and Discussion

1. Synthesis

At first, the substitution of 2-*p*-toluenesulfonyloxypropanenitrile $CH_3CH(OTs)CN$ with sodium nitrite was considered to make 2-nitropropanenitrile because 2-*p*-toluenesulfonyloxypropanenitrile is readily prepared by the reaction of acetaldehyde with *p*-toluenesulfonyl chloride and sodium cyanide[61] (equation 46). When 2-*p*-toluenesulfonyloxypropanenitrile was treated with sodium nitrite overnight, no product was isolated (equation 47). In order to understand why the reaction does not give the substitution product, we compared the reaction with that of α-haloesters and sodium nitrite because α-nitroesters and α-nitronitriles may have similar properties and close

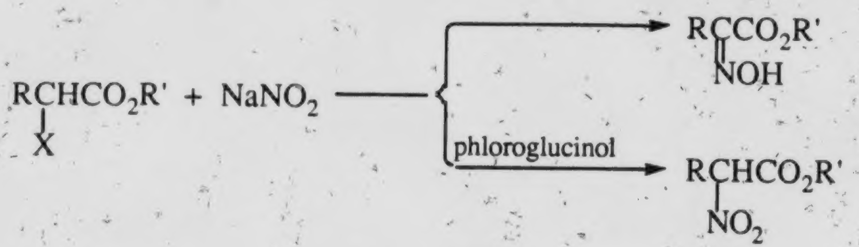


$$\mathrm{RCHO} + \mathrm{TsCl} + \mathrm{NaCN} \longrightarrow \mathrm{R}\underset{\mathrm{OTs}}{\underset{|}{\mathrm{C}}}\mathrm{HCN} + \mathrm{NaCl} \tag{46}$$



$$\mathrm{R}\underset{\mathrm{OTs}}{\underset{|}{\mathrm{C}}}\mathrm{HCN} + \mathrm{NaNO_2} \xcancel{\longrightarrow} \mathrm{R}\underset{\mathrm{NO_2}}{\underset{|}{\mathrm{C}}}\mathrm{HCN} \tag{47}$$

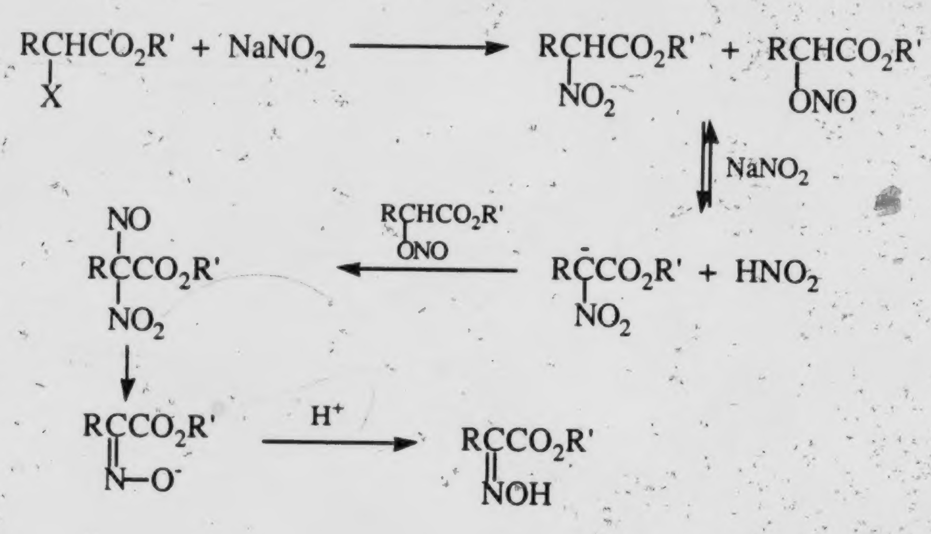
pKa values. Kornblum reported that the reaction of α-haloesters with sodium nitrite produces 2-oximinoesters (equation 48), but the same reaction in the presence of phloroglucinol (1,3,5-trihydroxybenzene) gives the substitution product α-nitroesters (equation 49).[62,63] This is because α-nitroesters are


RCHCO$_2$R'
X
NaNO$_2$
RCCO$_2$R'
NOH
phloroglucinol
RCHCO$_2$R'
NO$_2$

(48)

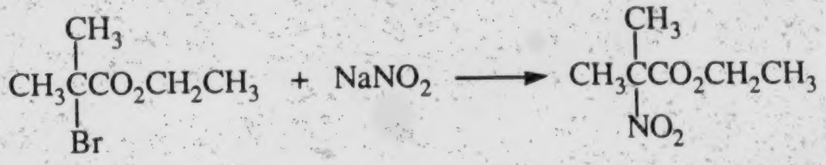
(49)

acidic and they can react with sodium nitrite to form the sodium salt of the α-nitroesters and nitrous acid. As shown in Scheme 13, a further reaction between the anion of α-nitroesters and nitrite esters produces the oximes. In the presence of phloroglucinol, the formation of the nitrite ester is inhibited.


RCHCO$_2$R'
X
NaNO$_2$
RCHCO$_2$R'
NO$_2$
RCHCO$_2$R'
ONO
NaNO$_2$
RCCO$_2$R'
NO$_2$
HNO$_2$
RCHCO$_2$R'
ONO
NO
RCCO$_2$R'
NO$_2$
RCCO$_2$R'
N–O$^-$
H$^+$
RCCO$_2$R'
NOH

Scheme 13. Reaction mechanism of α-haloesters with sodium nitrite without phloroglucinol.

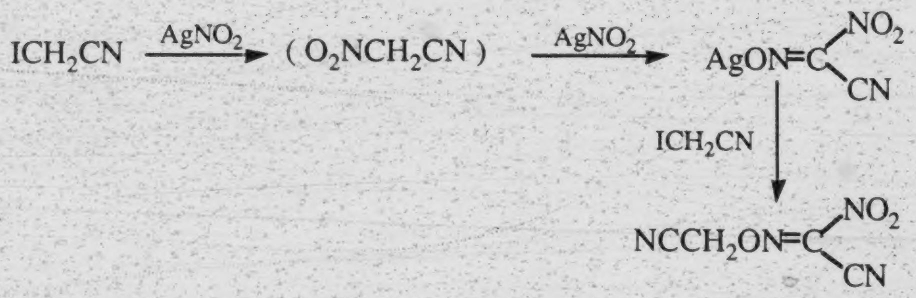
That this attribute of phloroglucinol is involved is shown by the production of ethyl 2-methyl-2-nitropropanoate in 78-91% yields without phloroglucinol being present[62] (equation 50). Here, the α-nitroester, being devoid of an α-hydrogen, cannot undergo the nitrosation reaction which converts α-nitroesters to α-oximinoesters. The nitrosation may happen for 2-nitropropanenitrile without the presence of phloroglucinol during the reaction of 2-*p*-toluenesulfonyloxypropanenitrile with sodium nitrite. However, when the reaction of 2-*p*-toluenesulfonyloxypropanenitrile with sodium nitrite was carried out in the presence of phloroglucinol overnight, still no product could be isolated and only a little starting material was recovered. Probably 2-nitropropanenitrile forms first and then decomposes immediately because it is an unstable compound.



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}CO_2CH_2CH_3 + NaNO_2 \longrightarrow CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}CO_2CH_2CH_3 \qquad (50)$$

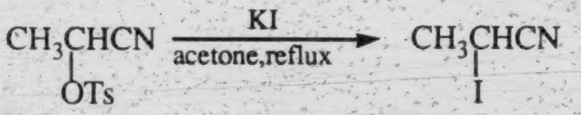
2-*p*-Toluenesulfonyloxyacetonitrile was also prepared and substitution attempted, but no nitroacetonitrile could be isolated. The presence of phloroglucinol has no effect on the substitution (equation 47, R = H).

Usually nitroalkanes are made by the reaction of haloalkanes with silver nitrite,[64] but the method cannot be used for the synthesis of nitroacetonitrile because nitroacetonitrile will react with nitrite ion further to form the *O*-cyanomethyl ether of nitroglyoxynitrile, which results from the reaction of 2-oximino-2-nitroacetonitrile with iodoacetonitrile[65] (Scheme 14). In the case of

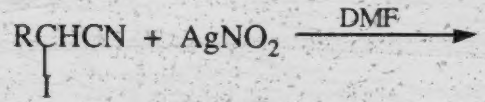


Scheme 14. Reaction mechanism of $AgNO_2$ with iodoacetonitrile.

2-iodopropanenitrile, the formation of the oxime is impossible. Thus we thought that the reaction of 2-iodopropanenitrile with silver nitrite might produce 2-nitropropanenitrile. 2-Iodopropanenitrile is easily made by refluxing a mixture of 2-*p*-toluenesulfonyloxypropanenitrile and potassium iodide in acetone in the dark for 24 hours (equation 51). 2-Iodonitropropanenitrile was identified by its NMR spectrum. The chemical shift of the methyl protons is located at δ 2.15 ppm as a doublet (J = 7 Hz) and that of the methine proton at δ 4.33 ppm as a quartet (J = 7 Hz). The crude product of 2-iodopropanenitrile was used directly without purification. No



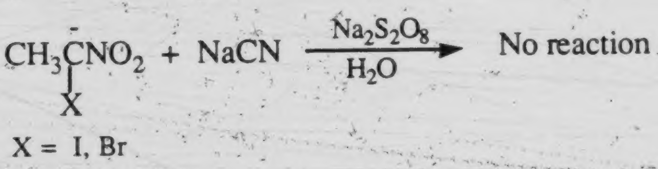
$$\underset{\text{OTs}}{\mathrm{CH_3CHCN}} \xrightarrow[\text{acetone,reflux}]{\text{KI}} \underset{\text{I}}{\mathrm{CH_3CHCN}} \qquad (51)$$



$$\underset{\text{I}}{\mathrm{RCHCN}} + AgNO_2 \xrightarrow{\text{DMF}} \text{No reaction} \qquad (52)$$

product was obtained for the reaction between 2-iodopropanenitrile and silver nitrite even after being stirred for six days (equation 52). 2-Iodopropanenitrile was recovered in about 30% yield.

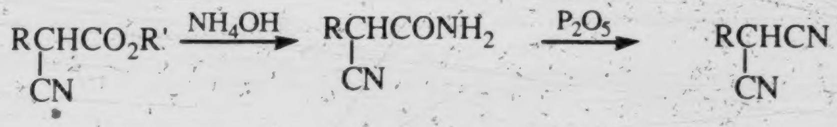
From the above results, it appears to be impossible to introduce a nitro group into the α-carbon of the substituted propanenitriles $CH_3CH(X)CN$ by the substitution with nitrite ion. We considered an alternative way to introduce a cyano group into the α-carbon of substituted nitroethanes $CH_3CH(X)NO_2$. As mentioned in the introduction, the ter Meer reaction is useful for the synthesis of 1,1-dinitroethane by the reaction of the sodium salt of 1-chloro-1-nitroethane with sodium nitrite (Scheme 2). Thus we considered a similar method to make 2-nitropropanenitrile by the reaction of the sodium salt of 1-bromo-1-nitroethane with sodium cyanide using sodium persulphate as an initiator (equation 53). However, the reaction in aqueous solution does not give any product. When 1-iodo-1-nitroethane was used, iodine was liberated during the reaction. We also tried the reaction in DMSO. Vigorous exothermic reactions were observed, but still no product was isolated. Cyanide ion is a poor electron donor. Thus no electron transfer reaction can take place for the above reaction.



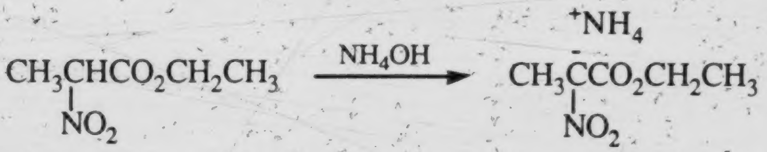
$$CH_3\underset{X}{\overset{-}{C}}NO_2 + NaCN \xrightarrow[H_2O]{Na_2S_2O_8} \text{No reaction} \qquad (53)$$

$$X = I, Br$$

We also intended to make 2-nitropropanenitrile by the dehydration of 2-nitropropanamide since 1,1-dicyano-compounds can be made by the dehydration of 2-cyanoamides with P_2O_5. 2-Cyanoamides are made by the reaction of 2-cyanoesters with ammonium hydroxide [66] (equation 54), but we were unable to get 2-nitropropanamide by the reaction of ethyl 2-nitropropanoate with ammonium hydroxide because the reaction produces the



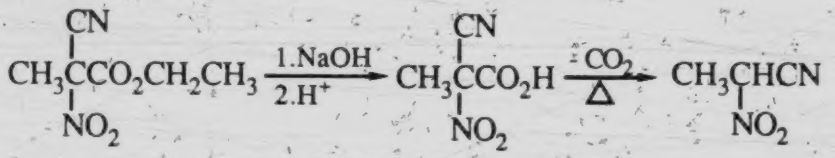
$$\mathrm{R\underset{\substack{|\\ CN}}{C}HCO_2R'} \xrightarrow{\mathrm{NH_4OH}} \mathrm{R\underset{\substack{|\\ CN}}{C}HCONH_2} \xrightarrow{\mathrm{P_2O_5}} \mathrm{R\underset{\substack{|\\ CN}}{C}HCN} \qquad (54)$$



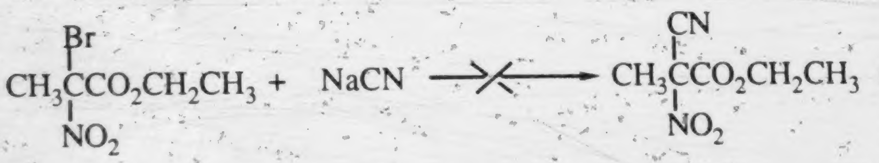
$$\mathrm{CH_3\underset{\substack{|\\ NO_2}}{C}HCO_2CH_2CH_3} \xrightarrow{\mathrm{NH_4OH}} \mathrm{CH_3\overset{\substack{{}^{+}NH_4\\ -}}{\underset{\substack{|\\ NO_2}}{C}}CO_2CH_2CH_3} \qquad (55)$$

ammonium salt of the 2-nitroester (equation 55). No further attempt was made to prepare 2-nitropropanenitrile by this way. This method may not be useful for the synthesis of 2-nitropropanenitrile because we found later that 2-nitropropanenitrile is an unstable compound and would decompose under the reaction conditions.

Since the above methods to synthesize 2-nitropropanenitrile failed, the hydrolysis of ethyl 2-cyano-2-nitropropanoate was considered. The decarboxylation of the corresponding carboxylic acid may give 2-nitropropanenitrile (equation 56).

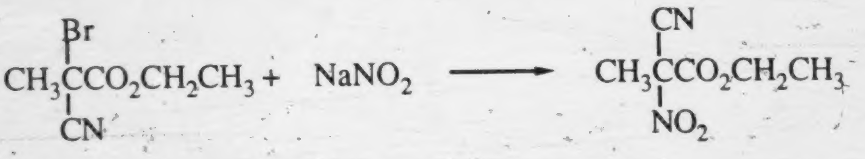


$$\mathrm{CH_3\overset{\substack{CN\\ |}}{\underset{\substack{|\\ NO_2}}{C}}CO_2CH_2CH_3} \xrightarrow[\mathrm{2.H^+}]{\mathrm{1.NaOH}} \mathrm{CH_3\overset{\substack{CN\\ |}}{\underset{\substack{|\\ NO_2}}{C}}CO_2H} \xrightarrow[\Delta]{\mathrm{-CO_2}} \mathrm{CH_3\underset{\substack{|\\ NO_2}}{C}HCN} \qquad (56)$$



$$CH_3\underset{NO_2}{\overset{Br}{C}}CO_2CH_2CH_3 + NaCN \not\longrightarrow CH_3\underset{NO_2}{\overset{CN}{C}}CO_2CH_2CH_3 \quad (57)$$

We tried to prepare ethyl 2-cyano-2-nitropropanoate by the reaction of ethyl 2-bromo-2-nitropropanoate with sodium cyanide (equation 57), but only a little starting material was recovered. As discussed above, sodium cyanide is a poor electron donor and thus the $S_{RN}1$ reaction may not happen between the 2-bromo-2-nitroester and cyanide ion. However, the reaction of ethyl 2-bromo-2-cyanopropanoate with sodium nitrite was reported to give a 55% yield of ethyl 2-cyano-2-nitropropanoate (equation 58).[67] We found that the

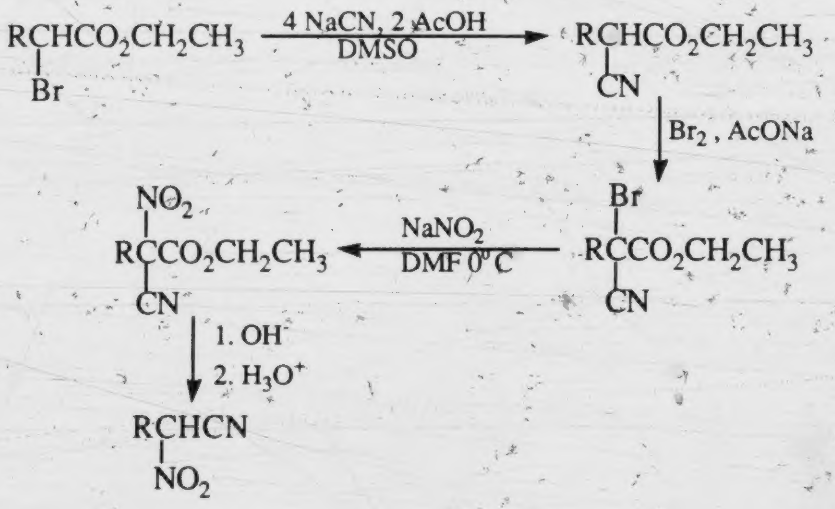


$$CH_3\underset{CN}{\overset{Br}{C}}CO_2CH_2CH_3 + NaNO_2 \longrightarrow CH_3\underset{NO_2}{\overset{CN}{C}}CO_2CH_2CH_3 \quad (58)$$

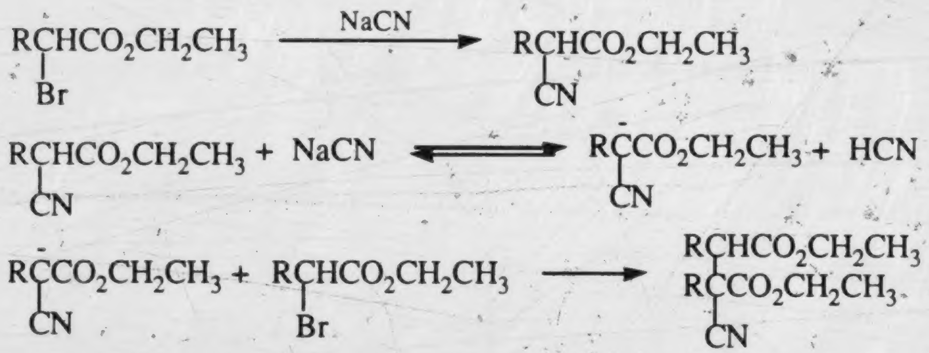
product ethyl 2-cyano-2-nitropropanoate is an unstable compound in the reaction mixture. If the reaction is stirred at room temperature overnight, the product ethyl 2-cyano-2-nitropropanoate will be decomposed by sodium nitrite. We were able to modify the reaction conditions by conducting the reaction under argon and at 0° C (the product 2-nitroester is stable at 0° C). Therefore, a better yield was obtained (> 90%).

In Scheme 15 ($R = CH_3$), the multiple-step synthesis of 2-nitropropanenitrile is shown. The reaction of ethyl 2-bromopropanoate with sodium cyanide in alcohol was reported to give about 20% yield of ethyl 2-

cyanopropanoate.[68] The major product is diethyl 2-cyano-2,3-dimethylsuccinate, which results from the reaction of the sodium salt of 2-cyanopropanoate with ethyl 2-bromopropanoate (Scheme 16). This is called the Franchimont reaction.[69]


RCHCO2CH2CH3
Br
4 NaCN, 2 AcOH
DMSO
RCHCO2CH2CH3
CN
Br2, AcONa
Br
RCCO2CH2CH3
CN
NaNO2
DMF 0°C
NO2
RCCO2CH2CH3
CN
1. OH-
2. H3O+
RCHCN
NO2

Scheme 15. Synthesis of 2-nitronitriles.


RCHCO2CH2CH3
Br
NaCN
RCHCO2CH2CH3
CN
RCHCO2CH2CH3 + NaCN
CN
RCCO2CH2CH3 + HCN
CN
RCCO2CH2CH3 +
CN
RCHCO2CH2CH3
Br
RCHCO2CH2CH3
RCCO2CH2CH3
CN

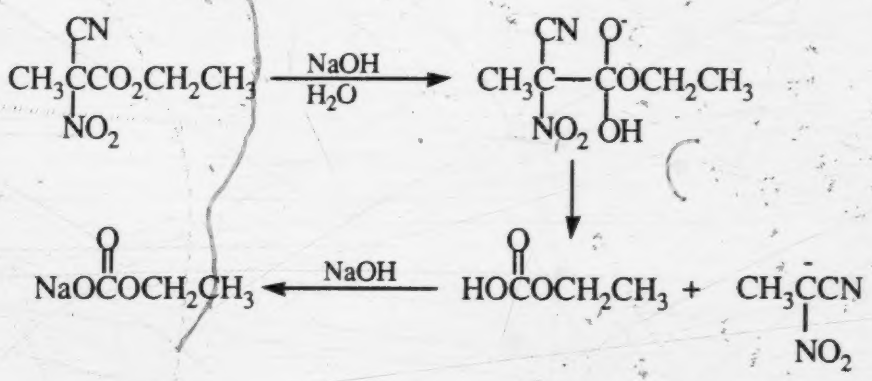
Scheme 16. Reaction mechanism of ethyl 2-bromoesters with NaCN.

We tried the reaction in DMSO because this solvent should increase the nucleophilicity of cyanide ion and thus the substitution will be accelerated.

However, the reaction of the 2-bromoester with cyanide ion in DMSO only gives a little higher yield (40%) of the 2-cyanoester. The major problem is the competition between the anion of the 2-cyanoester and cyanide ion. The competition could be avoided by using a buffer solution because the deprotonation of the 2-cyanoester may be reduced in the buffer (the pKa values of HCN and 2-cyanoesters are about 9 and 8 respectively). In fact, the reaction works well in the presence of two equivalents of acetic acid and four equivalents of sodium cyanide in DMSO. The yield of the product 2-cyanoester increases to 90%. The reaction will be discussed in detail in the fifth chapter.

The remaining steps (Scheme 15) for the synthesis of ethyl 2-cyano-2-nitropropanoate have been reported.[67] The sodium salt of 2-nitropropanenitrile was obtained directly by treatment with NaOH. To avoid the possible Nef reaction, the acidification of the sodium salt of 2-nitropropanenitrile should be carried out at 0° C and a weak acid such as acetic acid should be added slowly. Because 2-nitropropanenitrile is a stronger acid than AcOH, HCl should be added subsequently to adjust the pH to acidic before the isolation of the product with extraction. In this case, acetic acid functions as a buffer and prevents the Nef reaction. 2-Nitropropanenitrile was purified by distillation under vacuum below 35° C. The NMR spectrum of the compound shows a quartet at δ 5.40 ppm for the methine proton (J = 7 Hz) and a doublet at δ 2.03 ppm for the methyl protons (J = 7 Hz). The compound is unstable and insoluble in water, but its salt is soluble and stable in aqueous solution. At room temperature, the compound starts to decompose in about 1 h. as observed from color formation. The decomposition product has a strong acetic acid smell. No attempt was made to isolate the decomposition product.

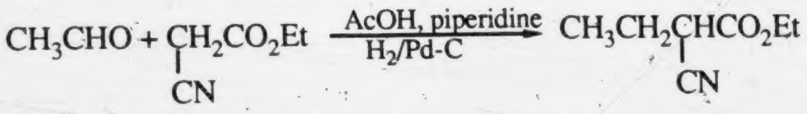
The hydrolysis of ethyl 2-cyano-2-nitropropanoate is extraordinary. Ethyl sodium carbonate was isolated by precipitation with ethanol, which indicates that the hydrolysis follows the way shown in Scheme 17. Because the anion of 2-nitropropanenitrile is very stable, instead of C-O bond cleavage, C-C bond cleavage is preferred as in the iodoform reaction. In addition, 2-cyano-2-nitroesters are reactive. The hydrolysis in methanol can be achieved by using sodium nitrite or sodium acetate as a base.



Scheme 17. Hydrolysis of ethyl 2-cyano-2-nitropropanoate.

We also made 2-nitrobutanenitrile by the same way as shown in Scheme 14 (R = Et). Ethyl 2-cyanobutanoate has been made by the esterification of 2-cyanobutanoic acid,[70,71] but the best way to make ethyl 2-cyanobutanoate is by the condensation of acetaldehyde with ethyl cyanoacetate under catalytic hydrogenation[72] (equation 59).

2-Nitrobutanenitrile was also purified by distillation. The NMR



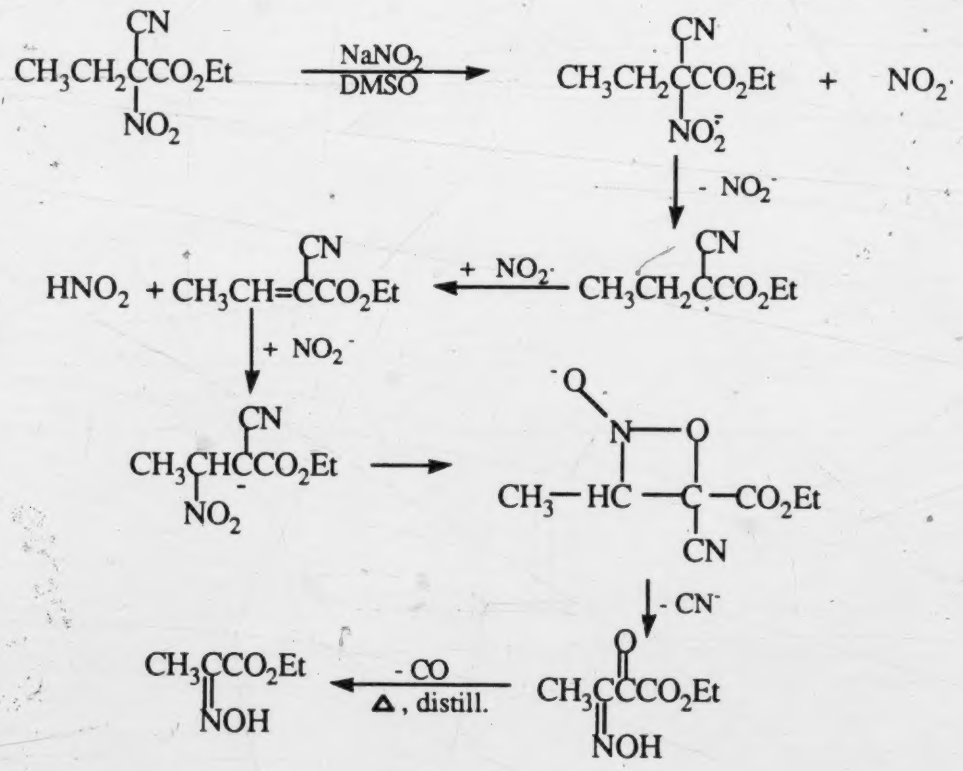
$$CH_3CHO + \underset{CN}{CH_2}CO_2Et \xrightarrow[H_2/Pd\text{-}C]{AcOH,\ piperidine} CH_3CH_2\underset{CN}{CH}CO_2Et \qquad (59)$$

spectrum of the compound shows a triplet for the methine proton at δ 5.24 ppm, and a quartet of doublets for the methylene protons at δ 2.26 ppm and a triplet for the methyl protons at δ 1.09 ppm (all coupling constants J = 7 Hz). 2-Nitrobutanenitrile is a fairly stable compound and can be stored at -10° C for 2 days without decomposition. It starts to decompose at room temperature in 2 h. as observed from color formation, but it is relatively stable in solution (the color forms in 24 h.). Both acid and amine are found to catalyze the decomposition as observed from the NMR spectrum in $CDCl_3$ solution. No attempt was made to investigate the decomposition product.

2. The decomposition mechanism of ethyl 2-cyano-2-nitrobutanoate

As mentioned in the synthesis of ethyl 2-cyano-2-nitropropanoate, if ethyl 2-bromo-2-nitropropanoate is stirred with sodium nitrite at room temperature overnight, the product ethyl 2-cyano-2-nitropropanoate will decompose. The decomposition is vigorous in DMSO if ethyl 2-cyano-2-nitropropanoate is allowed to react with sodium nitrite because a large amount of bubbles can be observed during the reaction. The gas is brown in color, which is probably NO_2. However, no reaction was observed at 0° C in DMF. We did not intend to isolate the decomposition product until we tried the reaction of ethyl 2-bromo-2-cyanobutanoate with sodium nitrite in DMSO. One of the decomposition products was isolated in 20% yield. The product was identified to be ethyl 2-oximinopropanoate. The compound melts at 96-97° C which is identical to the literature value[73] (97° C). The NMR spectrum of the oxime shows a singlet for the methyl protons at δ 2.03 ppm and a broad peak for the hydroxy proton at δ 5.63-6.25 ppm. The chemical shift of the ethyl group is located at δ 1.33 ppm as a triplet for the methyl protons and δ 4.25 ppm as a quartet for the methylene protons (J = 7 Hz).

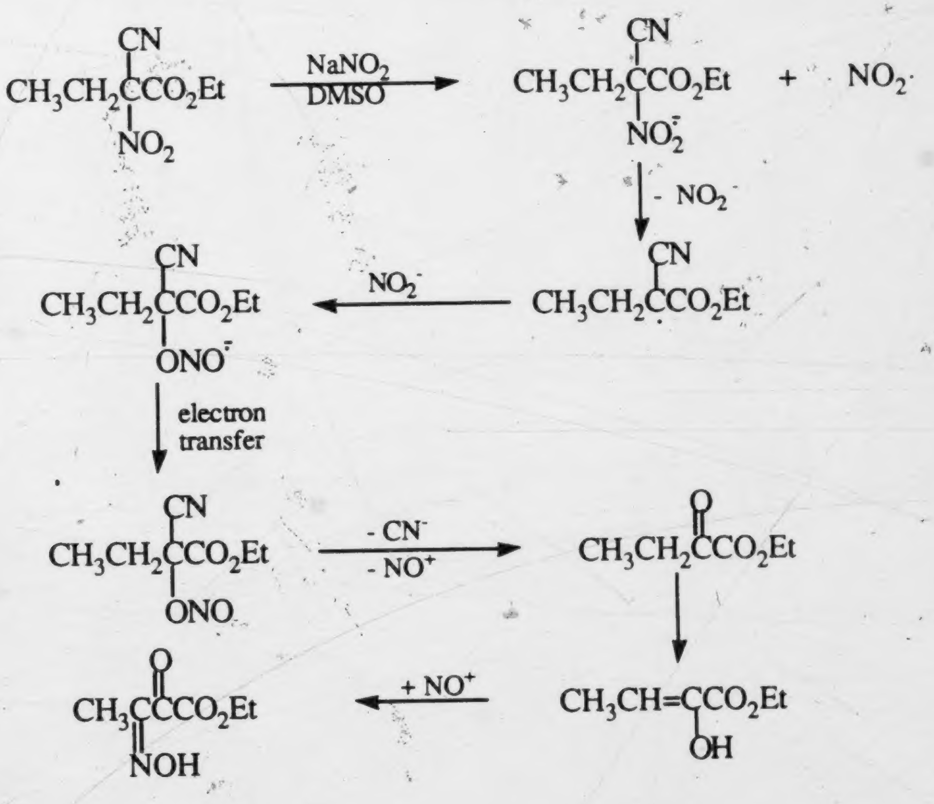
Two reaction mechanisms can be proposed as shown in Scheme 18 and 19. As shown in Scheme 18, the first step is the electron transfer from nitrite ion to the 2-cyano-2-nitroester. The resulting radical anion may lose a nitro



Scheme 18. One possible reaction mechanism for the reaction of ethyl 2-cyano-2-nitrobutanoate with $NaNO_2$.

group to form a radical of the 2-cyanoester. However, the nitrite radical may attack the radical of 2-cyanoester to form ethyl 2-cyanobutenoate and nitrous acid. The Michael addition of the alkene by nitrite ion and subsequent cyclization form an unstable intermediate, which may decompose to ethyl 3-oximino-2-oxobutanoate. Probably further decomposition during the distillation would result in the 2-oximinoester.

Another possible reaction mechanism is shown in Scheme 19. After the initiation, the resulting radical may combine with nitrite ion to form the nitrite ester, which may decompose to the 2-oxoester by elimination of cyanide ion


CN
CH₃CH₂CCO₂Et
NO₂
NaNO₂
DMSO
CN
CH₃CH₂CCO₂Et
NO₂⁻
+ NO₂·
- NO₂⁻
CN
CH₃CH₂CCO₂Et
NO₂⁻
CN
CH₃CH₂CCO₂Et
ONO⁻
electron transfer
CN
CH₃CH₂CCO₂Et
ONO
- CN⁻
- NO⁺
O
CH₃CH₂CCO₂Et
CH₃CH=CCO₂Et
OH
+ NO⁺
O
CH₃CCCO₂Et
NOH

Scheme 19. Another possible reaction mechanism for the reaction of ethyl 2-cyano-2-nitrobutanoate with $NaNO_2$.

and NO^+. The reaction of the enol of the 2-oxoester with nitrogen oxide cation or the nitrite ester may produce the 3-oximino-2-oxoester, which may decompose to the 2-oximinoester during the distillation. Both suggestions indicate that ethyl 3-oximino-2-oxobutanoate is the intermediate before it decomposes to the oxime.

In the first proposed mechanism (Scheme 18), ethyl 2-cyanobutenoate is believed to be an intermediate for the formation of ethyl 2-oximinopropanoate. A control experiment was made by the reaction of ethyl 2-cyanobutenoate with sodium nitrite in methanol and in DMSO, but in both solvents the alkene polymerized very easily even when sodium nitrite was used in large excess. The proposed mechanism is still possible because during the decomposition the concentration of the butenoate may be very low, which should lower the possibility for the polymerization.

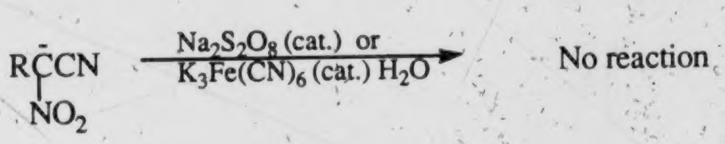
We also tried to monitor the reaction of methyl 2-cyano-2-nitrobutanoate with sodium nitrite by NMR in DMSO-d_6 and DMF-d_7. When DMF-d_7 was used as a solvent, several singlet peaks between δ 3.5 - 4.0 ppm were observed in half an hour. These peaks completely disappeared in 24 h. except the singlet at δ 3.63 ppm. The chemical shift of the ethyl group became complex and undistinguishable. In DMSO-d_6, the reaction only takes 160 min. as observed by the disappearance of the starting material. Also only the peak at δ 3.63 ppm remained 3 h. later in the region of δ 3.5-4.0 ppm. The product which shows the peak at δ 3.63 ppm may be the intermediate methyl 3-oximino-2-oxobutanoate.

In order to examine whether the decomposition is general for all 2-cyano-2-nitroesters, the reactions of methyl and ethyl 2-cyano-2-nitropentanoate with sodium nitrite were also tried. The pentanoate is less reactive than the butanoate and the major reaction in DMSO, which contains water, is the hydrolysis to 2-nitropentanenitrile. The hydrolysis may be avoided by introducing a big ester group which will increase the steric hindrance for the hydrolysis.

The reaction mechanism for the formation of the oxime still remains to be confirmed. Probably the best way to determine the reaction is to isolate every decomposition product, especially the the intermediate 3-oximino-2-oxoester.

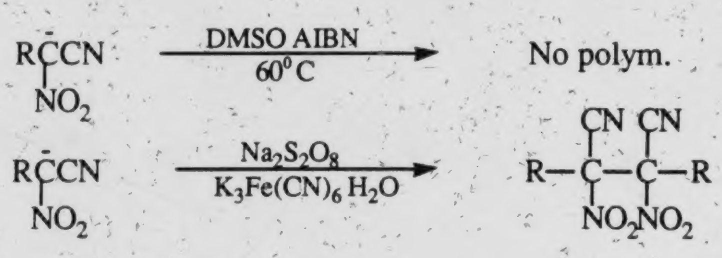
3. Attempted polymerization of 2-nitronitriles

After 2-nitropropanenitrile was obtained, we tried the polymerization of the salt in aqueous solution by using some oxidizing reagents such as sodium persulphate and potassium ferricyanide, but no apparent reaction was observed when only a small amount of the oxidizing reagent was used (equation 60). 2-Nitropropanenitrile could be recovered by acidification after the reaction. As discussed in the introduction, the $S_{RN}1$ reaction is slow in protic solvents because of a solvation effect. The effect may make the initiation for the polymerization more difficult. However, oxidizing reagents like



$$R\overset{-}{\underset{NO_2}{C}}CN \xrightarrow[K_3Fe(CN)_6\text{ (cat.) }H_2O]{Na_2S_2O_8\text{ (cat.) or}} \text{No reaction} \qquad (60)$$

potassium ferricyanide are insoluble in aprotic solvents. An alternative way to initiate the reaction was attempted using a radical reagent such as AIBN (2,2'-azobisisobutyronitrile). When the potassium salt of 2-nitropropanenitrile and a small amount of AIBN in DMSO were warmed to 60⁰ C, no product was obtained (equation 61). No starting material was recovered. Probably the anion is unstable and decomposes at 60⁰ C.



$$\underset{NO_2}{R\bar{C}CN} \xrightarrow[60^0\,C]{DMSO\ AIBN} \text{No polym.} \qquad (61)$$

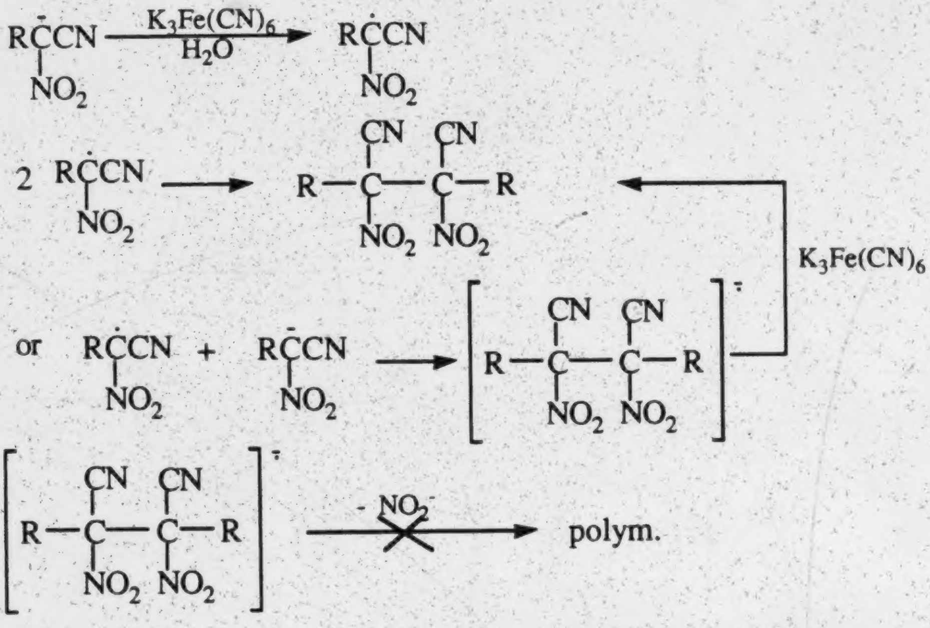
$$\underset{NO_2}{R\bar{C}CN} \xrightarrow[K_3Fe(CN)_6\ H_2O]{Na_2S_2O_8} R-\overset{CN}{\underset{NO_2}{C}}-\overset{CN}{\underset{NO_2}{C}}-R \qquad (62)$$

However, the anion of 2-nitropropanenitrile in aqueous solution can be oxidized by potassium ferricyanide to the dimer (equation 62, $R = CH_3$) when the oxidizing reagent is used in large excess. The reaction is very slow and only gives a 10% yield in 4 h. The yield was measured by the weight of the dimer. Because the dimer is insoluble in water and precipitates during the reaction, the product can be isolated easily by filtration. The crude product of the dimer was obtained in 50% yield in 2 days. Longer stirring does not give a higher yield. The dimer was purified by recrystallization from hexane-THF. The crystals were further purified by sublimation at 100⁰ C under vacuum. The dimer decomposes at 144⁰ C. The NMR spectrum of the dimer only shows two singlets at δ 2.36 and 2.39 ppm.

2-Nitrobutanenitrile was also prepared, but no reaction was observed for the reaction of the anion with a small amount of the oxidizing reagent (e.g.

$Na_2S_2O_8$). The sodium salt of 2-nitrobutanenitrile can be also oxidized by a large amount of potassium ferricyanide. The dimer was obtained in 45% yield (crude) in 3 days. It is a mixture of *meso* and *dl* isomers. The mixture can be easily separated by recrystallization from ethanol. One of the isomers crystallized from ethanol and was further purified by sublimation at 100° C under vacuum. This isomer decomposes at 142° C and its NMR spectrum shows a triplet for the methyl protons at δ 1.26 ppm, and a quartet of doublets at δ 2.28 ppm and a quartet of doublets at δ 2.86 ppm for the methylene protons (J = 7 and 14 Hz).

The residue, obtained after the recrystallization, contained mainly the other isomer (> 90%), as was determined from the NMR analysis. This isomer was also purified by recrystallization from ethanol and then

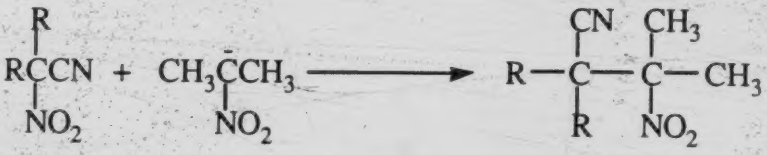


Scheme 20. Reaction mechanism of the anion of 2-nitronitriles with $K_3Fe(CN)_6$.

sublimation. This isomer melts at 118-120° C and its NMR spectrum shows a triplet for the methyl protons at δ 1.34 ppm, and two quartets of doublets at δ 2.36 and 2.78 ppm for the methylene protons (J = 7 and 14 Hz).

The dimer may arise from the coupling of two radicals of the 2-nitronitrile or from the coupling of a radical with an anion. As shown in Scheme 20, after the combination of the radical and the anion, the resulting radical anion of the dimer does not lose a nitro-group but transfers one electron to potassium ferricyanide immediately. The transfer of the electron to the oxidizing reagent may be a very fast process, which should prevent the polymerization. Furthermore, the precipitation of the dimer may also prevent the further reaction.

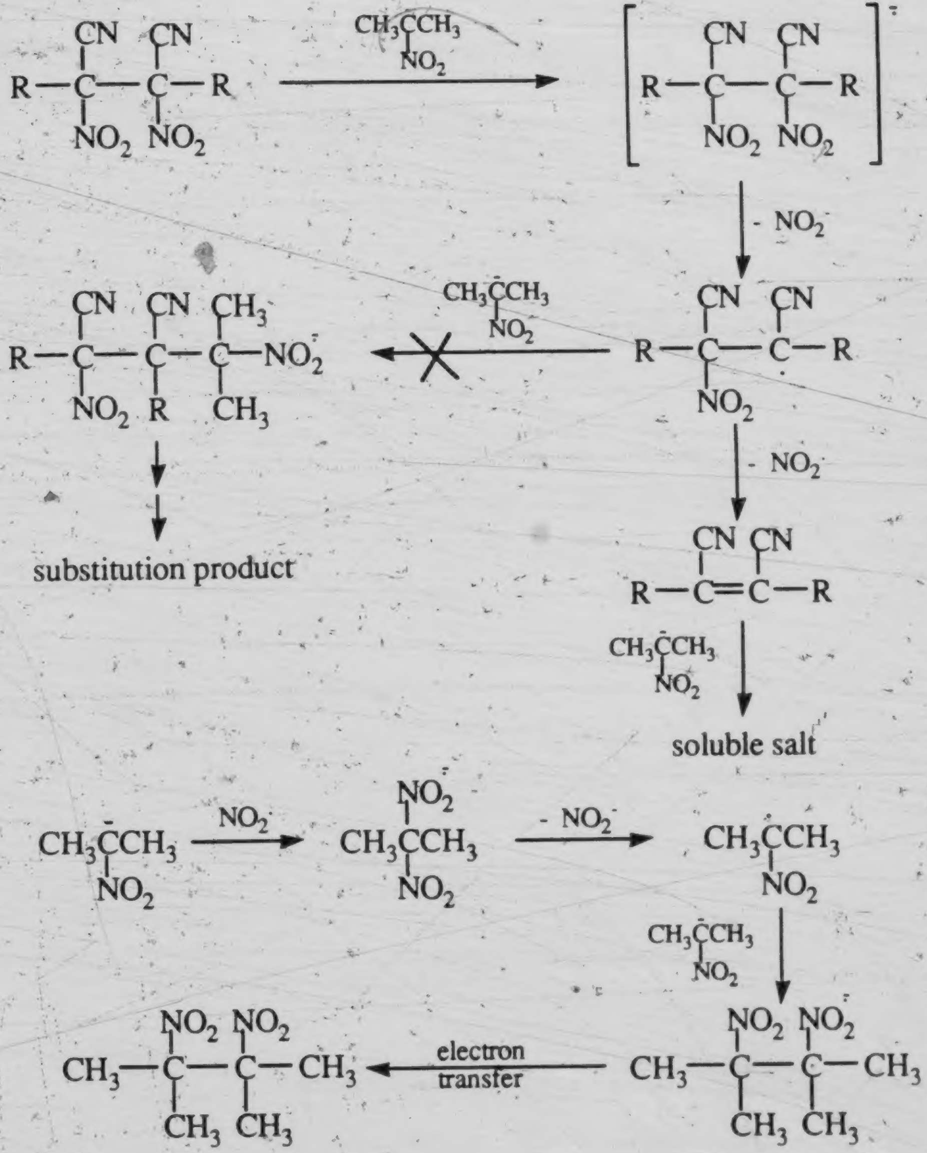
In order to determine whether 2-nitronitriles can be used for the polymerization, the reaction of the dimer with the lithium salt of 2-nitropropane was investigated. There should be no problem for the initiation



$$R\underset{NO_2}{\overset{R}{C}}CN + CH_3\underset{NO_2}{\overset{-}{C}}CH_3 \longrightarrow R-\underset{R}{\overset{CN}{C}}-\underset{NO_2}{\overset{CH_3}{C}}-CH_3 \qquad (63)$$

because the substitution of a tertiary α-nitronitrile with the lithium salt of 2-nitropropane gives a good yield of the substitution product[74] (equation 63). If the substitution reaction occurs between the dimer and the lithium salt of 2-nitropropane, then polymerization by the reaction of the dimer with the anion of 2-nitronitriles would be possible in a dipolar aprotic solvent. The polymerization can be initiated also by the lithium salt of 2-nitropropane

(Scheme 21). When 2,3-dicyano-2,3-dinitrobutane and two equivalents of the lithium salt of 2-nitropropane in HMPA were stirred overnight, 2,3-dimethyl-2,3-dinitrobutane was obtained in 75% yield, which was estimated from the

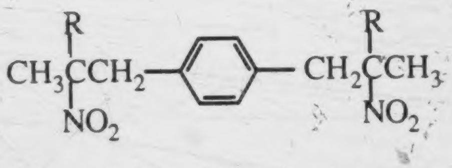

substitution product
soluble salt
electron transfer

Scheme 21. Reaction mechanism of the dimer with lithium 2-nitropropanate.

NMR spectrum using *p*-dimethoxybenzene as an internal standard. We were unable to isolate the elimination product, 2,3-dicyano-2-butene, probably because it reacts with lithium 2-nitropropanate further to form a soluble Michael adduct. The first initiation step does happen, but the resulting radical does not combine with the lithium salt of 2-nitropropane to let the chain propagate. Instead the elimination takes place. The strong tendency for the vicinal nitro-groups to eliminate to the alkene is known as observed in the reduction of the vicinal nitro-groups with sodium sulfide under illumination.[36] However, in the case of α,β-dicyano-α,β-dinitro compounds the elimination still occurs even without illumination. Because of the elimination reaction, the polymerization of 2-nitronitriles is impossible.

III. SYNTHESES AND REACTIONS OF MODEL COMPOUNDS FOR THE $S_{RN}1$ POLYMERIZATION

After the unsuccessful polymerization of 2-nitronitriles, we started to look for bifunctional compounds which can undergo the $S_{RN}1$ polymerization. As mentioned in the introduction, the reaction of gem-dinitro compounds with excess lithium nitronates (2 equivalents) always gives an excellent yield of the coupling product (e.g. equation 39). Therefore, we believed that there should be no problem in formation of the carbon carbon bond by $S_{RN}1$ polymerization of bifunctional compounds. Thus, 1,4-bis(2-nitropropyl)benzene (R = H) was prepared. The dilithium salt of the



R = H, NO_2, Li .

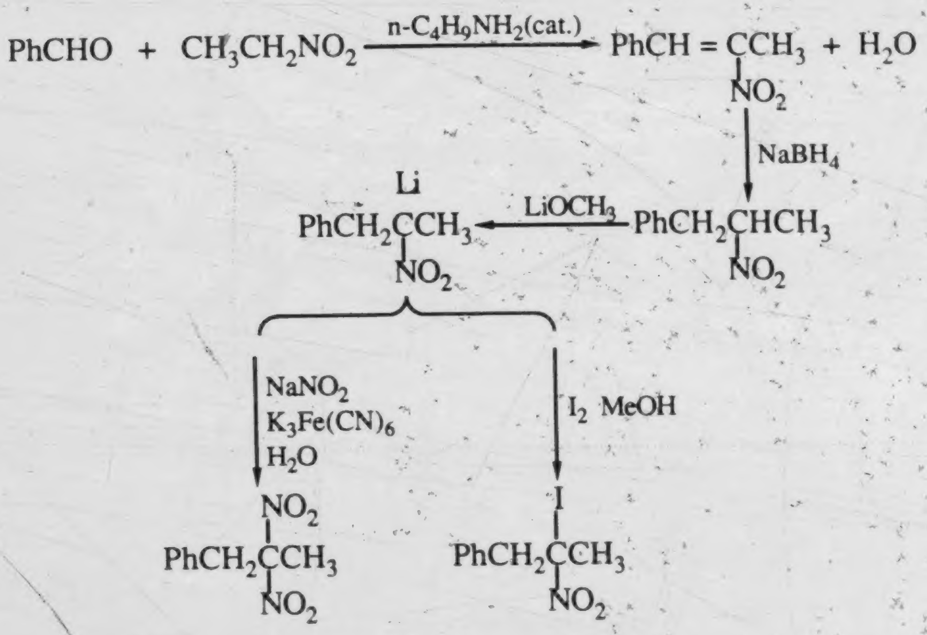
compound was used as an electron donor (R = Li) and 1,4-bis(2,2-dinitropropyl)benzene (R = NO_2) as an acceptor. However, as will be described in the next chapter, the reaction of the donor with one equivalent of the acceptor only produces a product with average molecular weight of 840 (trimer). Many efforts to increase the molecular weight by using different reaction conditions failed. In addition, the dilithium salt only dissolves slowly during the reaction. We also found that the product contained strong signals of the disproportionation product as indicated in the NMR spectrum by a peak for the methine proton of $RCH(NO_2)R'$ at δ 4.8-5.2 ppm. As mentioned in the introduction, the disproportionation is one of the termination processes for the $S_{RN}1$ reaction (e.g. equation 11). Thus the disproportionation could be the main reason why the polymerization gives trimer. In order to study and solve the above problems, the model compound 2-nitro-1-phenylpropane was prepared and the coupling reaction was investigated because this type of $S_{RN}1$ reaction was still unknown.

By studying the reaction, the coupling reaction using the tetraethylammonium nitronates with iodine was found to give a lower disproportionation yield. The reaction can be carried out in the presence of water. This discovery should be useful for the application of the $S_{RN}1$ reaction bacause an anhydrous condition is not necessary. We also explored other possible model compounds (electron donors and acceptors) for the $S_{RN}1$ polymerization. These compounds include 4,4'-disubstituted diphenyl sulfones and 2-cyanoesters. Some of these compounds may be potentially useful for the $S_{RN}1$ polymerization.

Results and Discussion

1. The synthesis and reactions of 2-nitro-1-phenylpropane and its lithium salt and 2,2-dinitro-1-phenylpropane

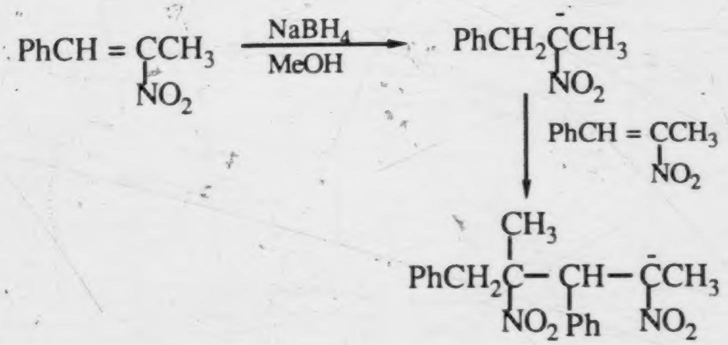
2-Nitro-1-phenyl-1-propene was prepared by the condensation of benzaldehyde with nitroethane in the presence of *n*-butylamine. The condensation proceeds very slowly at room temperature,[75] but the reaction in methanol under reflux gives about 55% yield.[76] We were successful in increasing the yield to 85% by using the procedure for the preparation of 1-(2-methoxy)phenyl-2-nitropropene in toluene.[77] The synthesis is illustrated in Scheme 22. 2-Nitro-1-phenylpropane has been made recently by the reduction


PhCHO + CH3CH2NO2
n-C4H9NH2(cat.)
PhCH = CCH3 + H2O
NO2
NaBH4
PhCH2CHCH3
NO2
LiOCH3
Li
PhCH2CCH3
NO2
NaNO2
K3Fe(CN)6
H2O
I2 MeOH
NO2
PhCH2CCH3
NO2
I
PhCH2CCH3
NO2

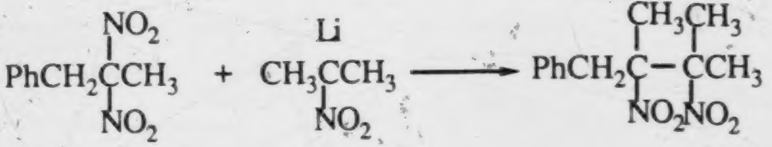
Scheme 22. Synthesis of 2-nitro-1-phenylpropane and its derivatives.

with sodium borohydride in methanolic THF solution (MeOH:THF = 1:10).[78] This method can prevent the Michael type dimerization reaction[79] as shown in equation 64, which happens when the reaction is carried out in methanol. 2,2-Dinitro-1-phenylpropane was made by using a general procedure for the preparation of gem-dinitro compounds.[15]

As expected, the reaction of 2,2-dinitro-1-phenylpropane with two equivalents of the lithium salt of 2-nitropropane in HMPA gives the substitution product in 94% yield (equation 65). The compound was purified



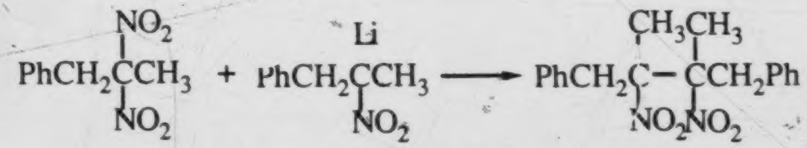
$$\mathrm{PhCH{=}C(NO_2)CH_3 \xrightarrow[MeOH]{NaBH_4} PhCH_2\bar{C}(NO_2)CH_3 \xrightarrow{PhCH=C(NO_2)CH_3} PhCH_2C(CH_3)(NO_2){-}CH(Ph){-}\bar{C}(NO_2)CH_3} \qquad (64)$$



$$\mathrm{PhCH_2C(NO_2)_2CH_3 + CH_3C(Li)(NO_2)CH_3 \longrightarrow PhCH_2C(CH_3)(NO_2){-}C(CH_3)(NO_2)CH_3} \qquad (65)$$

by recrystallization from hexane. The crystals melt at 119-120° C. The NMR spectrum of the compound shows three singlets for the methyl protons at δ 1.40, 1.74 and 1.95 ppm, and two doublets for the methylene protons at δ 3.28 and 3.90 ppm (J = 7 Hz).

The coupling reaction of 2,2-dinitro-1-phenylpropane with two equivalents of the lithium salt of 2-nitro-1-phenylpropane in HMPA also gives the dimer in excellent yield (equation 66). The dimer is a mixture of *dl* and



$$\mathrm{PhCH_2C(NO_2)_2CH_3 + PhCH_2C(Li)(NO_2)CH_3 \longrightarrow PhCH_2C(CH_3)(NO_2){-}C(CH_3)(NO_2)CH_2Ph} \qquad (66)$$

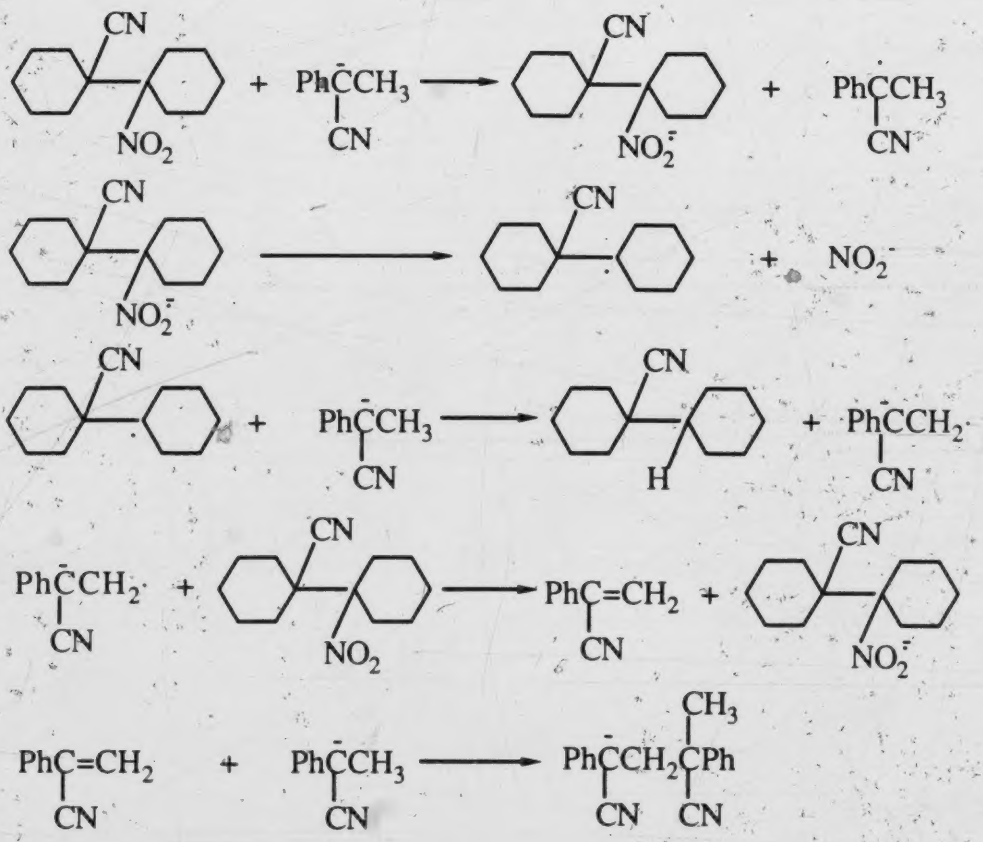
ratio 1 : 2 yield 94%
1 : 1 79%

dl and *meso*

meso isomers, which can be easily separated by the extraction with benzene. One of the isomers which is soluble in benzene was purified by recrystallization from hexane. The crystals melt at 188-190^0 C. The NMR spectrum of the isomer shows a singlet for the methyl protons at δ 1.38 ppm and two doublets for the methylene protons at δ 2.70 and 4.08 ppm (J = 7 Hz). The above benzene insoluble material was collected and purified by recrystallization from THF. These crystals decompose at 230^0 C. This isomer has different chemical shifts in the NMR spectrum. The methyl protons are located at δ 1.58 ppm and the methylene protons at δ 3.08 and 4.04 ppm as a doublet (J = 7 Hz). Probably the latter is the *meso* isomer because it has a higher melting point.

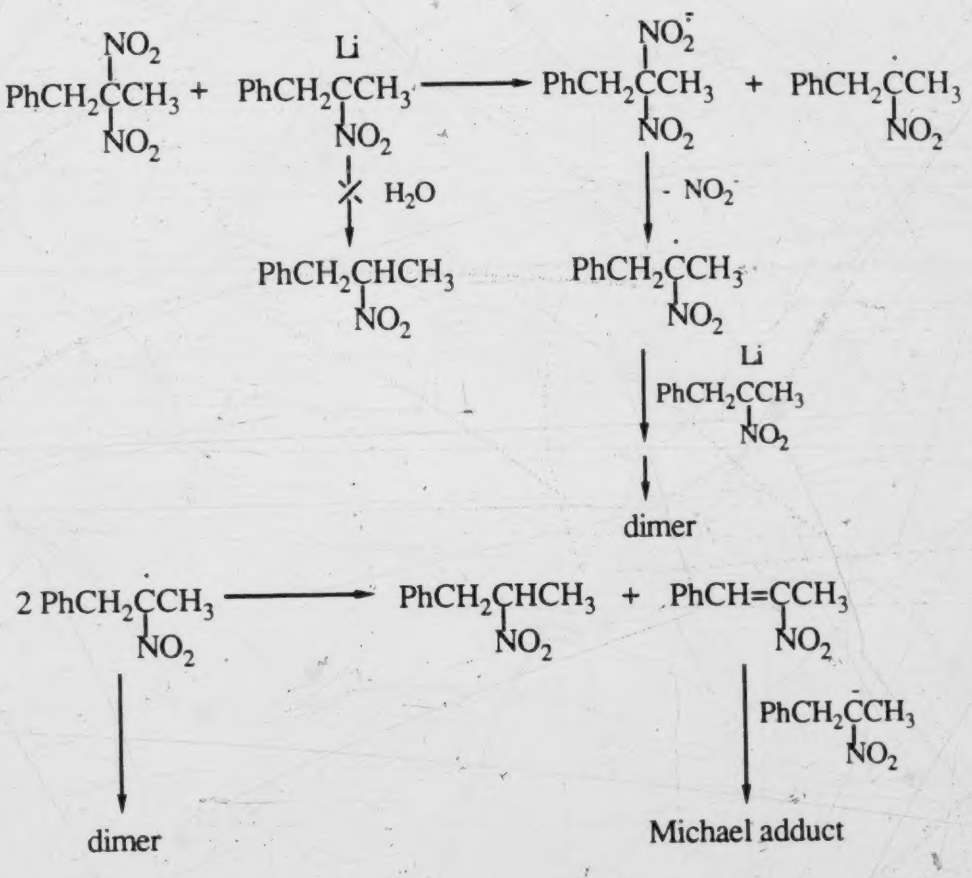
The first thing to be solved for the polymerization was the disproportionation, which is one of the termination processes for the $S_{RN}1$ reaction. If the disproportionation occurs between two radicals, then it should be possible to reduce the reaction by increasing the reactivity of the nitronates because the chance for the coupling reaction between a radical and an anion will increase. However, the disproportionation may happen by the reaction of the radical and the anion. This has been shown by Kornblum in the reaction of α-methylbenzyl cyanide anion with the ß-nitronitrile (Scheme 23).[80a] The disproportionation between the anion and the radical produces α-cyanostyrene, which will react with the anion to form the Michael adduct.

By studying the coupling reaction of the model compound, the magnitude of the disproportionation reaction can be estimated. HMPA was used as a solvent for the reaction because the dimer is more soluble. The same result can be obtained for the reaction in DMSO. No solvent dependence was observed for the reaction. We expected that the reaction would give a low



Scheme 23. Reaction mechanism of α-methylbenzyl cyanide anion with the β-nitronitrile.

disproportionation yield when two equivalents of the lithium salt of 2-nitro-1-phenylpropane were allowed to react with 2,2-dinitro-1-phenylpropane under illumination for 20 min. However, one of the disproportionation products 2-nitro-1-phenylpropane was obtained in 5% yield. The disproportionation yield was estimated by the integration of the signal of the methine proton of the NMR spectrum using *p*-dimethoxybenzene as an internal standard. The possibility that 2-nitro-1-phenylpropane comes from the lithium salt was excluded by a blank test, which was performed by dissolving the same amount of the lithium salt in water and working this up in the same way. The disproportionation is illustrated in Scheme 24. We were unable to isolate the



Scheme 24. Reaction mechanism of the disproportionation.

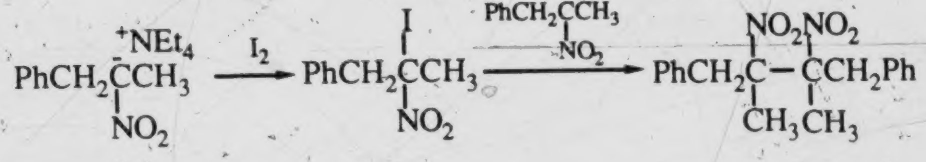
other part of the disproportionation product probably because it reacts with the lithium salt to form a soluble Michael adduct. As mentioned earlier, this Michael addition can take place in methanol. The addition may also happen in DMSO or HMPA.

The disproportionation yield (5%) is already significant for the coupling reaction. This is a surprising result. The lithium salt of 2-nitro-1-phenylpropane is soluble during the reaction. The chance for the radical to react with the anion should be high because there is excess anion in the solution during the reaction. Low reactivity of the lithium salt or the possible reaction between the radical and the anion should be responsible for the disproportionation.

If the disproportionation comes from the reaction between the radical and the anion, then it is impossible to prevent the reaction no matter how reactive the anion is. On the other hand, if the disproportionation results from the reaction of two radicals, the disproportionation can be decreased by increasing the reactivity of the anion because higher reactivity of the anion means higher possibility for the reaction between the anion and the radical. We can prove that the disproportionation mainly comes from the reaction of two radicals because a lower disproportionation yield is observed when a more reactive anion is used for the coupling reaction.

As mentioned in the introduction, the tetraalkylammonium salt of a nitro compound is more reactive than the lithium salt as observed in the reaction of the tetrabutylammonium salt of 2-nitropropane with α,*p*-dinitrocumene and *p*-nitrobenzyl bromide.[28,29] As will be discussed later, we also found that the the coupling reaction is faster when the tetraethylammonium salt of 2-nitro-1-phenylpropane and 2-iodo-2-nitro-1-phenylpropane (or iodine) are used for the coupling reaction.

Thus the disproportionation yield should be decreased for the reaction of the tetraethylammonium salt of 2-nitro-1-phenylpropane and iodine if the disproportionation results from the reaction of two radicals. Indeed, the reaction of the tetraethylammonium salt of 2-nitro-1-phenylpropane with one equivalent of iodine (in 2:1 molar ratio) in HMPA only gives a 2% disproportionation yield as measured by the same method mentioned above (equation 67). It should be emphasized that the yield was obtained when there



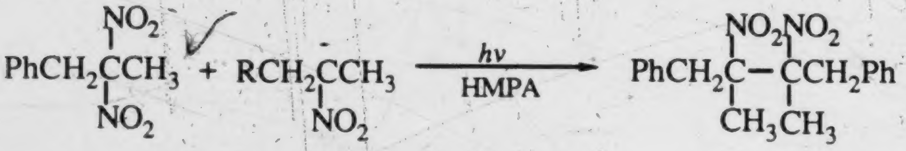
$$PhCH_2\overset{^+NEt_4}{\underset{NO_2}{\bar{C}}}CH_3 \xrightarrow{I_2} PhCH_2\overset{I}{\underset{NO_2}{C}}CH_3 \xrightarrow{PhCH_2\overset{-}{\underset{NO_2}{C}}CH_3} PhCH_2\overset{NO_2}{\underset{CH_3}{C}}-\overset{NO_2}{\underset{CH_3}{C}}CH_2Ph \qquad (67)$$

is no excess anion during the reaction. The disproportionation was less than 0.5% for the reaction of the ammonium salt with iodine (in 3:1 molar ratio). Therefore, the disproportionation yield can be reduced to 2% with one equivalent of reagent and further down to 0.5% by using excess ammonium salt.

It seems that both factors (two radicals coupling and the coupling between the radical and the anion) contribute to the disproportionation. In the case of the lithium salt, the reactivity is lower than the ammonium salt. The chance for two radicals to disproportionate should be higher although the lithium salt is used in excess. However, the disproportionation yield can be only reduced to 0.5% by using the ammonium salt and iodine. Both the ammonium salt and 2-iodo-2-nitro-1-phenylpropane are very reactive compounds. The 0.5% disproportionation yield may result from the reaction of the radical with the anion. Hence, for the lithium salt the disproportionation mainly results from the reaction of two radicals. For the polymerization a little excess anion is required in order to reduce the possible disproportionation.

In order to obtain a high molecular weight polymer from bifunctional monomers like in condensation polymerization, the monomers must be used in 1:1 ratio. Therefore, an equivalent of the electron donor and acceptor should be used for the $S_{RN}1$ polymerization, but this may result in a problem for the polymerization because there is no excess anion in the solution and the chance for the disproportionation of two radicals should increase. Thus low molecular weight polymer may be produced.

While studying the coupling reaction of the model compound, we found another problem which may influence the polymerization. When one equivalent of the lithium salt of 2-nitro-1-phenylpropane is used for the coupling reaction with 2,2-dinitro-1-phenylpropane (1:1 ratio) under illumination for 20 min, the reaction is only 75% - 80% complete (the ratio of the starting material 2,2-dinitro-1-phenylpropane and the dimer is about 1:4 in the product) as determined from the NMR spectrum (equation 68). The



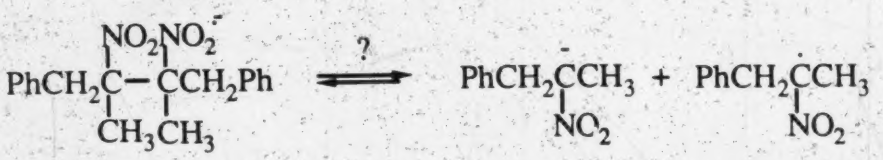
$$\mathrm{PhCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_3} + \mathrm{RCH_2\overset{-}{\underset{NO_2}{C}}CH_3} \xrightarrow[\text{HMPA}]{h\nu} \mathrm{PhCH_2\overset{NO_2}{\underset{CH_3}{C}}-\overset{NO_2}{\underset{CH_3}{C}}CH_2Ph} \quad (68)$$

both in 1:1 ratio

R	time	yield
Ph	20 min.	75%
Ph	5 h.	80%
H	20 min.	80%

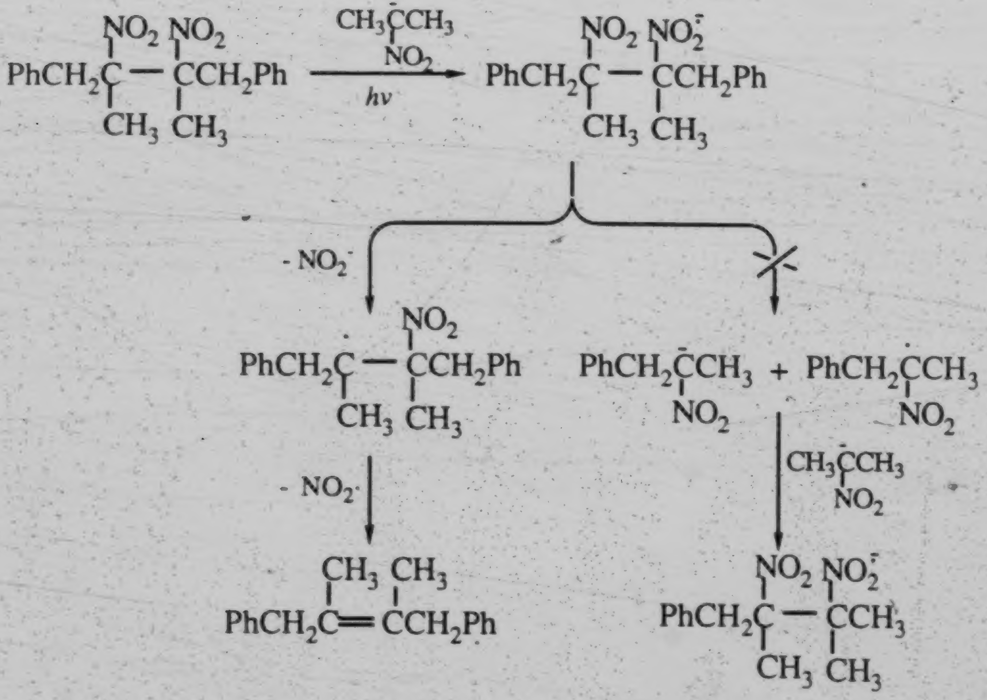
reaction was worked up by precipitation with water. The precipitate was analyzed from its NMR spectrum. In addition, when the reaction is illuminated for a long time (5 hours), the ratio only changes a little. The ratio of the starting material and the product is about 1:5. We did not try the reaction of the lithium salt of 2-nitropropane with 2,2-dinitropropane when both are used in 1:1 ratio, but we have tried the reaction of the lithium salt of 2-nitropropane with one equivalent of 2,2-dinitro-1-phenylpropane. In this case, the reaction is only about 80% complete in 20 min. under illumination. We call this a ratio effect.

The ratio effect should be the second factor which influences the polymerization. At first, we speculated that a reversible reaction was responsible for the above result as shown in equation 69 because the ratio of

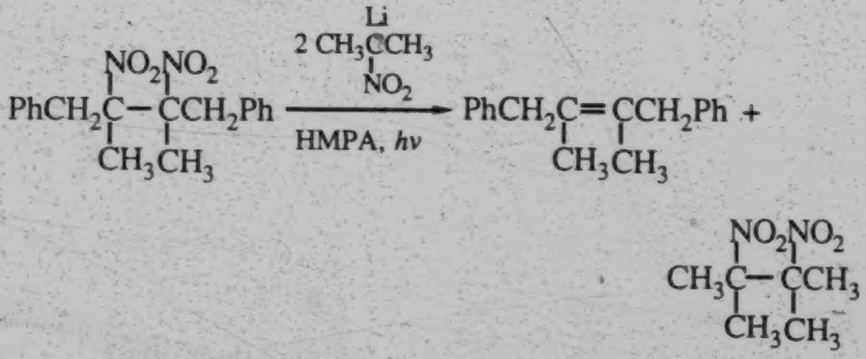


$$\mathrm{PhCH_2\underset{CH_3}{\overset{NO_2}{C}}-\underset{CH_3}{\overset{NO_2^{\dot{-}}}{C}}CH_2Ph} \xrightleftharpoons{?} \mathrm{PhCH_2\underset{NO_2}{\overset{-}{C}}CH_3} + \mathrm{PhCH_2\underset{NO_2}{\overset{\cdot}{C}}CH_3} \qquad (69)$$

the product and the starting material only changes a little with longer illumination, Furthermore, no elimination product was observed which usually happens with long illumination in the presence of excess lithium salt. As shown in Scheme 25, if the reversible reaction could occur, then a radical of 2-nitro-1-phenylpropane should be produced. The radical could react with the lithium salt of 2-nitropropane to give the cross coupling product 2,3-dimethyl-2,3-dinitro-1-phenylpropane, which can be detected by the NMR spectrum. We tried the reaction by using the dimer and two equivalents of the



Scheme 25. Reaction of the dimer with the lithium salt 2-nitropropane.

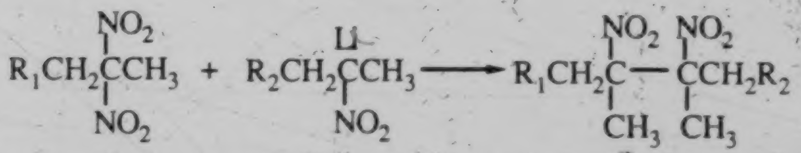


$$PhCH_2\underset{CH_3}{\overset{NO_2}{C}}-\underset{CH_3}{\overset{NO_2}{C}}CH_2Ph \xrightarrow[\text{HMPA, } h\nu]{2\ CH_3\overset{Li}{C}(NO_2)CH_3} PhCH_2\underset{CH_3}{C}=\underset{CH_3}{C}CH_2Ph + CH_3\underset{CH_3}{\overset{NO_2}{C}}-\underset{CH_3}{\overset{NO_2}{C}}CH_3 \qquad (70)$$

lithium salt of 2-nitropropane under illumination (equation 70), but only the signals of the elimination product 2,3-dimethyl-1,4-diphenyl-2-butene and 2,3-dimethyl-2,3-dinitrobutane were detected in the NMR spectrum (the reaction mechanism will be discussed later). The NMR spectrum of 2,3-dimethyl-2,3-dinitrobutane shows only one singlet at δ 1.72 ppm, while 2,3-dimethyl-1,4-diphenyl-2-butene shows two singlets for the methyl protons at δ 1.64 and 1.72 ppm, two singlets for the methylene protons at δ 3.46 and 3.52 ppm. Thus the ratio effect may result from the low reactivity of both donor and acceptor but not from the reversible reaction. The reason why the chain reaction cannot go to completion when 2,2-dinitro-1-phenylproprane and the lithium salt of 2-nitro-1-phenylpropane or the lithium salt of 2-nitropropane are used in 1:1 ratio still remains unknown. As will be discussed later, both the tetraethylammonium salt of 2-nitro-1-phenylpropane and 2-iodo-2-nitro-1-phenylpropane have higher reactivity. The effect was not observed for the reaction of the tetraethylammonium salt of 2-nitro-1-phenylpropane with 2-iodo-2-nitro-1-phenylpropane in acetonitrile and was observed to be small for the reaction in HMPA and DMSO. Thus it can be concluded that the ratio effect can be avoided by using more reactive electron acceptors and donors or by using excess amount of the donor when a lithium nitronate is used.

The third factor which influences polymerization is the reactivity. If the reactivity of both electron donor and acceptor is low, the polymerization should take a long time. We have shown that the disproportionation mainly results from the reaction of two radicals. If the reactivity of the anion is low, then the reaction between the anion and radical is slow. In fact, the lithium salt is not very reactive because even in the presence of two equivalents of anion, the reaction still gives a 5% disproportionation yield. At the beginning, this problem was not noticed until the coupling reaction of the model compound was investigated.

As mentioned by Kornblum,[80b] the reaction between 2,2-dinitropropane with the lithium salt of 2-nitropropane takes only 2 min. (equation 71, R_1, R_2 = H). The lithium salt of 2-nitropropane and 2,2-dinitropropane must be very reactive compounds. In order to study the reactivity of the model compound, we monitored the reaction of 2,2-dinitro-1-phenylpropane with the lithium salt of 2-nitropropane (1:2 ratio) in HMPA by TLC (eluant 1% methanol in chloroform). It was found that the reaction takes about 1 h. (R_1 = Ph, R_2 = H). The same product can be obtained by the reaction of 2,2-dinitropropane with the lithium salt of 2-nitro-1-phenylpropane (1:2 ratio) in 1 h. (R_1 = H, R_2 = Ph). It is also possible to monitor the reaction of 2,2-dinitro-1-phenylpropane with the lithium salt of 2-nitro-1-phenylpropane (1:2 ratio) by TLC (eluant benzene:hexane:methanol =



$$R_1CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_3 + R_2CH_2\overset{Li}{\underset{NO_2}{C}}CH_3 \longrightarrow R_1CH_2\overset{NO_2}{\underset{CH_3}{C}}-\overset{NO_2}{\underset{CH_3}{C}}CH_2R_2 \qquad (71)$$

R_1	R_2	time
H	H	2 min.*
Ph	H	1 h.
H	Ph	1 h.
Ph	Ph	5 h.
Ph	Ph	15 min. (illumination)
Ph	Ph	2 h. (50°C)

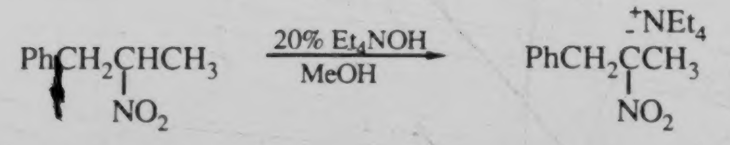
*The reaction was conducted in DMSO. No detail reaction conditions were mentioned.

78:20:2). The reaction requires 5 h. as observed by the disappearance of the starting material 2,2-dinitro-1phenylpropane (R_1, R_2 = Ph). It is not known why the presence of phenyl groups slows down the coupling reaction.

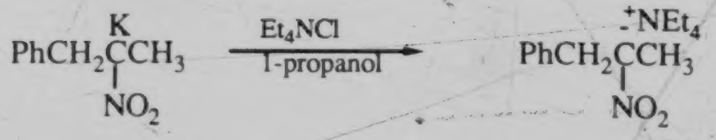
From the above result, the formation of the C-C bond from the reaction of lithium nitronates with gem-dinitro compounds is slow. We believe that the C-C bond formation for the reaction between 1,4-bis(2,2-dinitropropyl)benzene and the dilithium salt of 1,4-bis(2-nitropropyl)benzene is even slower. This slow reaction is why the polymerization only gives the trimer.

The $S_{RN}1$ reaction (also the disproportionation) is always accelerated by light. The coupling reaction between 2,2-dinitro-1-phenylpropane and the lithium salt of 2-nitro-1-phenylpropane (1:2 ratio) only takes 15 min. with illumination by a 15 w fluorescent light. The reaction rate is thus 20 times faster than the reaction without illumination (5 h.). On the other hand, the reaction is not very sensitive to temperature and still requires 2 h. at 50° C.

As observed in the reaction of the tetrabutylammonium salt of 2-nitropropane with α,*p*-dinitrocumene and *p*-nitrobenzyl bromide, the ammonium salt is much more reactive than the lithium salt.[28,29] We tried to make the tetraethylammonium salt of 2-nitro-1-phenylpropane by using 20% aqueous solution of tetraethylammonium hydroxide (equation 72), but we could not isolate the pure salt. The attempt to remove water by drying with molecular sieves leads to the decomposition probably because of the presence of oxygen. Another method was also tried by the reaction of the potassium salt of 2-nitro-1-phenylpropane with anhydrous tetraethylammonium chloride



$$PhCH_2\underset{NO_2}{C}HCH_3 \xrightarrow[MeOH]{20\%\ Et_4NOH} PhCH_2\overset{^{-+}NEt_4}{\underset{NO_2}{C}}CH_3 \qquad (72)$$

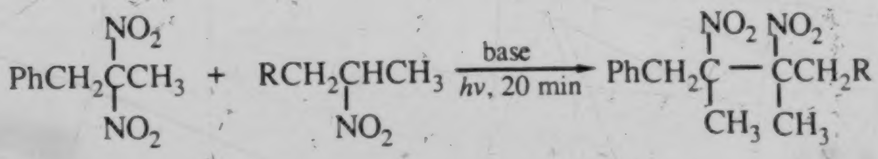


$$PhCH_2\overset{K}{\underset{NO_2}{C}}CH_3 \xrightarrow[1\text{-propanol}]{Et_4NCl} PhCH_2\overset{^{-+}NEt_4}{\underset{NO_2}{C}}CH_3 \qquad (73)$$

in 1-propanol (equation 73). No reaction takes place in methanol. The driving force must be the precipitation of potassium chloride because KCl is only slight soluble in 1-propanol, and will be precipitated during the reaction. However, this method only gave impure product because it contained some tetraethylammonium chloride and 1-propanol as observed from the NMR spectrum.

Because it is not easy to obtain the pure ammonium salt, the coupling reaction in the presence of water was studied. Surprisingly, the presence of water (10-15% in the solution) has little influence for the $S_{RN}1$ reaction because the coupling reaction of the tetraethylammonium salt of 2-nitro-1-phenylpropane, which is generated *in situ* by one equivalent of Et_4NOH (20% solution), with 2,2-dinitro-1-phenylpropane (in 3:1 ratio) gives an excellent yield (equation 74, R = Ph) with illumination for 20 min. The reaction of the ammonium salt of 2-nitropropane with 2,2-dinitro-1-phenylpropane also affords the substitution product in almost quantitative yield under the same reaction condition (equation 74, R = H). Because the ammonium salt is insoluble in dichloromethane or in benzene in the presence of water, the reaction can be only carried out in a solvent which is miscible with water such as acetonitrile or DMSO.

Actually, the coupling reaction can be simplified by using sodium hydroxide solution as a base (equation 74). Thus two equivalents of the



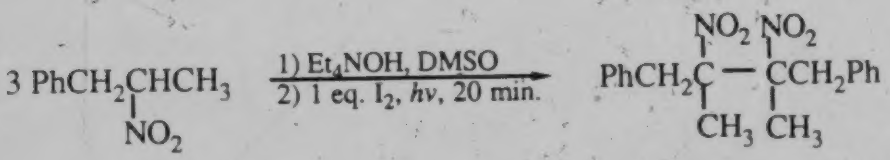
$$\mathrm{PhCH_2C(NO_2)_2CH_3} + \mathrm{RCH_2CH(NO_2)CH_3} \xrightarrow[h\nu,\ 20\ \mathrm{min}]{\mathrm{base}} \mathrm{PhCH_2C(NO_2)(CH_3)}-\mathrm{C(NO_2)(CH_3)CH_2R} \quad (74)$$

in 1:2 ratio

base	R	yield
Et_4NOH	H	91%
	Ph	91%
NaOH	Ph	91%

sodium salt of 2-nitro-1-phenylpropane are generated by sodium hydroxide solution in HMPA. The reaction of the sodium salt with 2,2-dinitro-1-phenylpropane gives the dimer in 91% yield. This simple procedure could be used for the coupling reactions of other nitro-compounds.

The procedure can be simplified further for the coupling reaction by using iodine with the tetraethylammonium salt. Thus the tetraethylammonium salt of 2-nitro-1-phenylpropane (three equivalents) was generated by 20% Et_4NOH in HMPA. The coupling reagent iodine (one equivalent) was added subsequetly. After illumination for 20 min., the dimer was isolated by prercipitation with water in 94% yield (equation 75). The order of adding



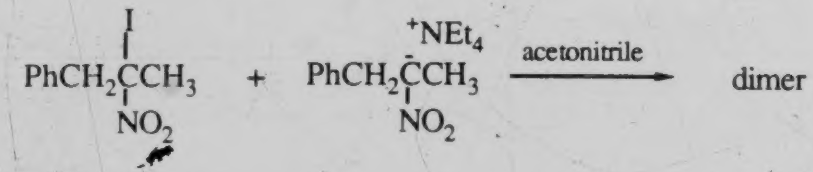
$$3\ \mathrm{PhCH_2CH(NO_2)CH_3} \xrightarrow[2)\ 1\ \mathrm{eq.}\ I_2,\ h\nu,\ 20\ \mathrm{min.}]{1)\ \mathrm{Et_4NOH,\ DMSO}} \mathrm{PhCH_2C(NO_2)(CH_3)}-\mathrm{C(NO_2)(CH_3)CH_2Ph} \quad (75)$$

reagents is important. If iodine is added before Et_4NOH, Et_4NOH will react with iodine first (form iodide ion and the salt of iodic acid) and thus the coupling reaction only gives the dimer in low yield. To avoid the reaction of iodine with tetraethylammonium hydroxide, the nitro compound should be converted to its tetraethylammonium salt first by using exactly one equivalent amount of Et_4NOH.

It is very difficult to determine the concentration of Et_4NOH. We tried to titrate Et_4NOH by using 1 N HCl and the concentration obtained (the labled concentration of commercially available product is 20% by weight) was 19.2%. When this concentration was used to convert 2-nitro-1-phenylpropane into the ammonium salt, the reaction of the ammonium salt with iodine (in 2:1 molar ratio) only gave a low yield of the dimer (< 75%). We tried to determine the concentration of Et_4NOH by the coupling reaction of 2-nitro-1-phenylpropane in the presence of various amounts of Et_4NOH with iodine (2:1 ratio). We found that the concentration at 18.5% gave the highest yield of dimer (> 85%). It should be pointed out that the reaction is very sensitive to the quantity of Et_4NOH. If a little more Et_4NOH is used, the reaction yield will drop dramatically because the excess Et_4NOH would consume iodine first before the coupling reaction can occur. If less Et_4NOH is used, the reaction will not go to completion because there is not enough of the ammonium salt inside. In this case, a little 2-iodo-2-nitro-1-phenylpropane was observed in the product from the NMR spectrum. On the other hand, if 2-nitro-1-phenylpropane is used in excess (e.g. 2.2 equivalents), there is no problem with the coupling reaction using iodine (a little excess Et_4NOH can be used).

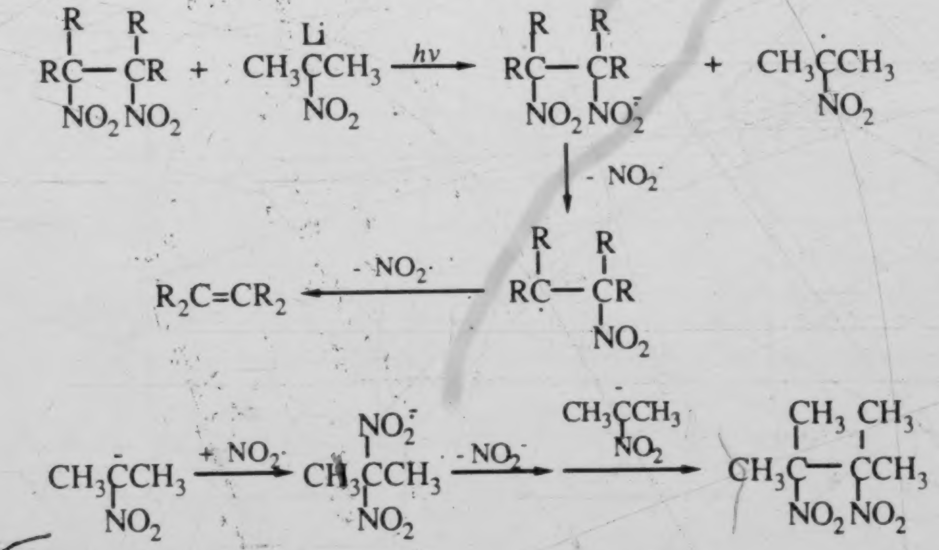
By studying the coupling reaction of the ammonium salt with iodine, we also found that the ammonium salt of 2-nitro-1-phenylpropane is more reactive than the lithium salt of 2-nitro-1-phenylpropane. The coupling reaction of the iodo compound with the tetraethylammonium salt of 2-nitro-1-phenylpropane in acetonitrile (containing 10% water) takes only 30 min. in laboratory light (the reaction of 2,2-dinitro-1-phenylpropane with the lithium salt of 2-nitro-1-phenylpropane normally takes 5 h.). The same reaction requires only less than 5 min. under illumination. On the other hand, the reaction of 2,2-dinitro-1-phenylpropane with the ammonium salt in acetonitrile is very slow. The reaction is only 16% complete after illumination for 5 hours. Attempts to initiate the reaction by using iodine were unsuccessful (only 30% yield in 8 h.). Thus the reactivity of the gem dinitro-compound is much lower than the iodo compound.

Protic solvents like methanol cannot be used for the $S_{RN}1$ reaction because of the solvation effect.[30-32] Thus dipolar aprotic solvents such as DMSO are required for $S_{RN}1$ reactions if a lithium nitronate is used because the lithium salt is more soluble in these solvents than in benzene or dichloromethane. The reaction of the tetrabutylammonium nitronates in the benzyl and p-nitrocumyl systems in benzene and dichloromethane was also reported.[28,29] However, these reactions were always carried out under anhydrous conditions. We found that this is not necessary. We have already shown that the reaction in the presence of water (even 10-15%) still gives an excellent yield of the substitution product. Even dipolar solvents are not required for the reaction. The reaction in acetonitrile or in THF proceeds faster and also gives an excellent yield (equation 76).

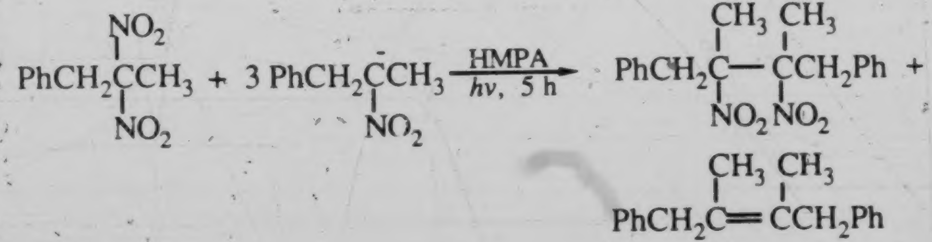


$$\mathrm{PhCH_2\underset{NO_2}{\overset{I}{C}}CH_3} + \mathrm{PhCH_2\underset{NO_2}{\overset{^+NEt_4}{\bar{C}}}CH_3} \xrightarrow{\text{acetonitrile}} \text{dimer} \qquad (76)$$

Although illumination speeds up the coupling reaction greatly, it also causes the elimination of the vicinal nitro groups. As mentioned earlier, the vicinal nitro groups can be eliminated to give a double bond by sodium sulfide with illumination.[36] We found that the lithium salt of 2-nitropropane can be also used as an electron donor for the elimination with illumination. Thus the alkene 2,3-dimethyl-1,4-diphenyl-2-butene is produced by the reaction of the dimer 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane with the lithium salt of 2-nitropropane (1:4 ratio) for 5 h., but 2,3-dimethyl-2,3-dinitrobutane (57% yield) is also produced, which results from the processes as indicated in Scheme 26. No attempt was made to measure the yield of the alkene. When the pure *dl* or *meso* dimers are used for the reaction, the alkene isolated is a mixture of *trans* and *cis* isomers in 1:1 ratio as observed from the NMR spectrum, which indicates that the elimination has no stereoselectivity. If 2,2-dinitro-1-phenylpropane and three equivalents of the anion of 2-nitro-1-phenylpropane in HMPA are illuminated for 5 h., a mixture of the dimer and 2,3-dimethyl-1,4-diphenyl-2-butene is produced (equation 77). This is because the dimer is unstable under illumination in the presence of



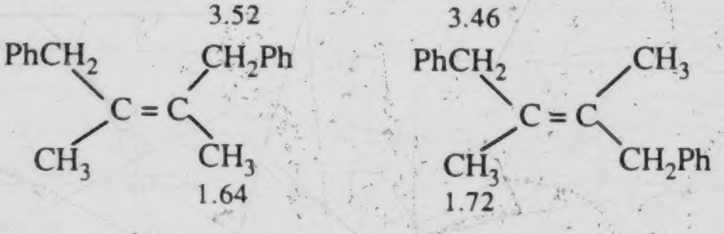
Scheme 26. Reaction of vicinal dinitro compounds with lithium 2-nitropropanate.

 (77)

the excess lithium salt. Thus the presence of the anion causes the elimination. We did not intend to isolate and measure the yield. However, without illumination no elimination reaction takes place if the reaction is carried out at room temperature for 24 h.

The alkene, 2,3-dimethyl-1,4-diphenyl-2-butene, was purified by distillation. One of the isomers crystallizes out in the distillate. The crystals can be further purified by recrystallization from pentane and melt at 48-50°C.

Figure I. The structures of *cis* and *trans*-2,3-dimethyl-1,4-diphenyl-2-butene


3.52
PhCH2
CH2Ph
CH3
CH3
1.64
3.46
PhCH2
CH3
CH3
CH2Ph
1.72

cis *trans*

Figure II. The structure of the anion of 2-methyl-1-phenylallyl

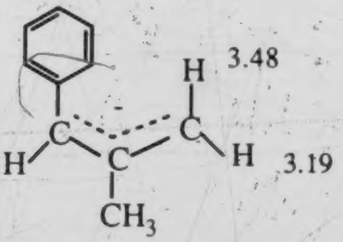
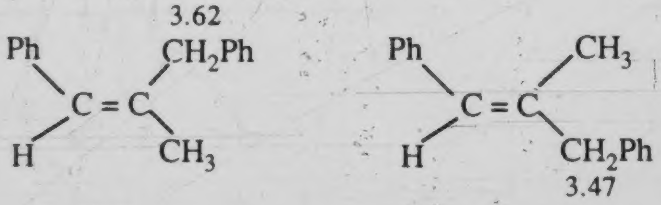

H
3.48
H
H
3.19
CH3

Figure III. The structures of *cis* and *trans*-1,3-diphenyl-2-methylpropene


3.62
Ph
CH2Ph
H
CH3
Ph
CH3
H
CH2Ph
3.47

cis *trans*

The NMR spectrum of this isomer shows a singlet for the methyl protons at δ 1.72 ppm and a singlet for the methylene protons at δ 3.46 ppm (Figure I). This isomer is believed to be the *trans* isomer. After recrystallization, the filtrate contains mainly the other isomer and it is a liquid. The NMR spectrum of the liquid isomer shows a singlet at δ 1.64 ppm for the methyl protons and a singlet at δ 3.52 ppm for the methylene protons. We tried to identify the solid and liquid isomers by their NMR spectrum. From the chemical shifts of the *trans* and the *cis* isomers, it seems that the protons of both methyl groups in the *trans* isomer are deshielded by the remote benzene rings. On the other hand, the methylene protons of the *cis* isomer (liquid) are deshielded by both benzene rings, which causes the chemical shift to lower field. There is no reported chemical shift for *trans* and *cis* 1,4-diphenyl-2-butene, but the anion of 2-methyl-1-phenylallyl shows the similar pattern as illustrated in Figure II.[82a,b] The methylene protons of *trans*- and *cis*-1,3-diphenyl-2-methylpropene also show distinct chemical shifts in the NMR spectrum (Figure III).[82c,d] By comparing the chemical shift, the solid alkene is probably the *trans* isomer and the liquid *cis* isomer.

Solubility was the fourth problem to be solved. The dilithium salt of 1,4-bis(2-nitropropyl)benzene is only slightly soluble in HMPA or DMSO. Organolithium compounds are associated in hydrocarbon solvents.[83] For the bifunctional compound, the dilithium salt should be polymeric and this is why the dilithium salt has so low a solubility in HMPA. As mentioned earlier, the disproportionation depends on the concentration of the donor and the reactivity of the donor and the acceptor. During the polymerization, the dilithium salt only dissolves slowly. This low solubility should increase the chance of disproportionation because the concentration of the anion becomes lower.

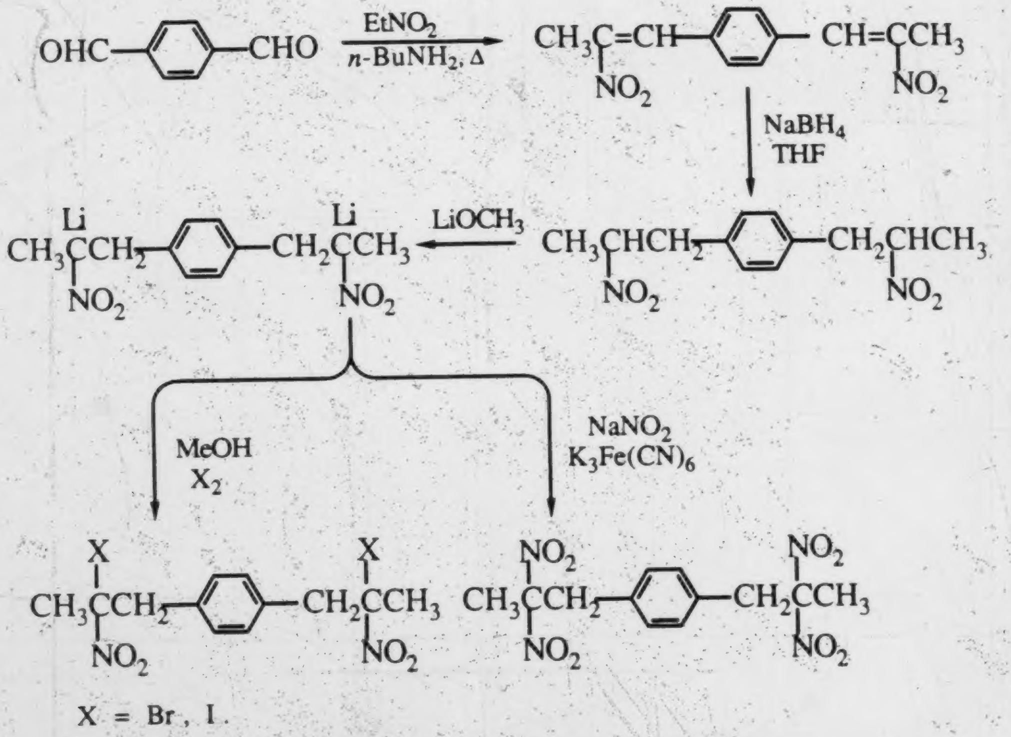
Addition of water into HMPA or DMSO may increase the solubility of the dilithium salt, but at the same time, the presence of water may decrease the reactivity for the $S_{RN}1$ reaction because of the solvation effect. As mentioned earlier, the tetraethylammonium salts show very high reactivity towards the

$S_{RN}1$ reaction. We considered that the diammonium salt might solve the solubility problem. However, the solubility problem still remains to be solved because we found later that the pure di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene is insoluble in HMPA and DMSO. The solubility problem will be discussed in the next chapter.

2. Synthesis and reactions of 1,4-bis(2-nitropropyl)benzene and its gem dinitro compound and the halo compound

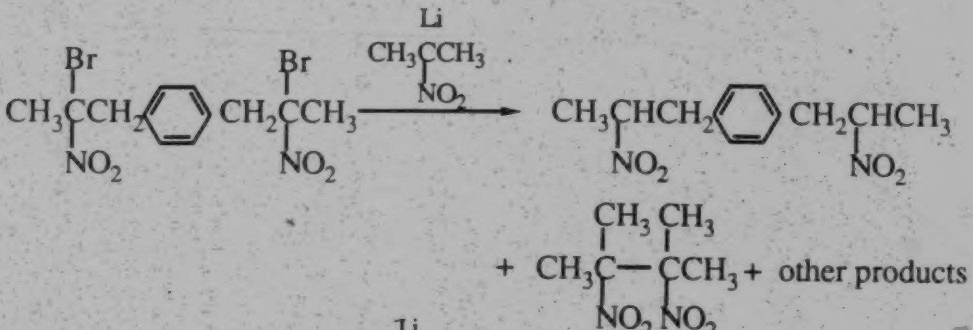
The compound 1,4-bis(2-nitropropyl)benzene can be made by using the procedure for the preparation of the mono-substituted compound (Scheme 27). The condensation of terephthaldicarboxaldehyde with nitroethane at room temperature takes a long time and gives 1,4-bis(2-nitro-1-propenyl)benzene in low yield,[84] but the condensation under reflux in nitroethane for 24 h. gives the alkene in 74% yield.[85] Reduction of the alkene by using sodium borohydride in methanolic THF solution (THF:MeOH = 10:1) gives 1,4-bis(2-nitropropyl)benzene in good yield. 1,4-Bis(2,2-dinitropropyl)benzene is also made in 60% yield by using the general procedure for the preparation of *gem*-dinitro compounds. A better yield could be obtained if a large excess sodium nitrite were used since this could reduce the possible side reactions such as dimerization, which result from the nitronate reacting with the resulting gem-dinitro product. 1,4-Bis(2-halo-2-nitropropyl)benzenes were made by the reaction of the dilithium salt with bromine or iodine in methanol.

In order to test the $S_{RN}1$ reaction for the compound, we tried the reaction of the lithium salt of 2-nitropropane with 1,4-bis(2-bromo-2-

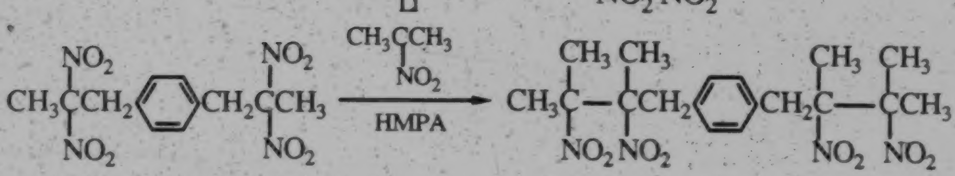


Scheme 27. Synthesis of 1,4-bis(2-nitropropyl)benzene and its derivatives.

nitropropyl)benzene and 1,4-bis(2,2-dinitropropyl)benzene. However, it is impossible to monitor the reaction by TLC to know how long the reaction takes because it is difficult to distinguish the disubstituted and mono-substituted product. When 1,4-bis(2-bromo-2-nitropropyl)benzene was stirred with the lithium salt of 2-nitropropane in HMPA for 24 h., a mixture was obtained. The mixture contained a little 1,4-bis(2-nitropropyl)benzene and 2,3-dimethyl-2,3-dinitro-butane as observed from the NMR spectrum. The cross bromination of the lithium salt takes place (equation 78). On the other hand, 1,4-bis(2,2-dinitropropyl)benzene can react with the lithium salt of 2-nitropropane to give the substitution product (equation 79). The reaction was



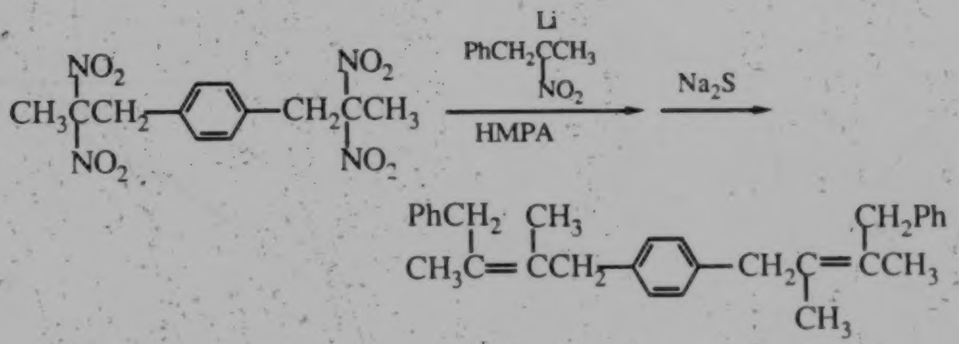
(78)



(79)

carried out in lab light to avoid the elimination of the vicinal dinitro-groups by the lithium salt of 2-nitropropane. The product is insoluble in DMSO at room temperature. It was purified by recrystallization from nitroethane. The compound decomposes at 240° C.

1,4-Bis(2,2-dinitropropyl)benzene also reacts with the lithium salt of 2-nitro-1-phenylpropane. The product is even more insoluble in common organic solvents. We were unable to get satisfactory elemental analysis even after recrystallization from DMSO-nitroethane five times. The possible product, 1,4-bis(2,3-dimethyl-2,3-dinitro-4-phenylbutyl)benzene, was reduced with sodium sulfide directly in HMPA under illumination (equation 80). One of the elimination products was isolated in 28% yield by collecting the precipitate after water was added. The isomer was purified by



(80)

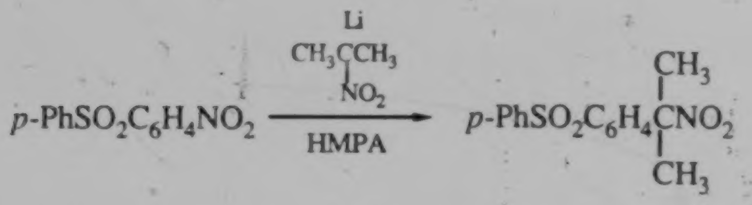
recrystallization from hexane. The NMR spectrum of the alkene, 1,4-bis(2,3-dimethyl-4-phenyl-2-butenyl)benzene, shows a singlet for the methyl protons at δ 1.74 ppm and two singlets for the methylene protons at δ 3.42 and 3.44 ppm. This isomer is probably the *trans, trans*-alkene because the chemical shifts are close to those of methyl and methylene protons of *trans*-2,3-dimethyl-1,4-diphenyl-2-butene. We tried to isolate other isomers by extraction with dichloromethane. After removal of the solvent, the crude product still contained isomers as observed from the NMR spectrum. The methyl protons were located at δ 1.66, 1.74 and 1.80 ppm. The methylene protons were located at δ 3.44, 3.46, 3.50, 3.54, 3.68, 3.72 ppm. The residue has a strong hydrogen sulfide smell and changes to a red color gradually. Purification of the mixture by recrystallization was unsuccessful.

3. Other electron donors or acceptors

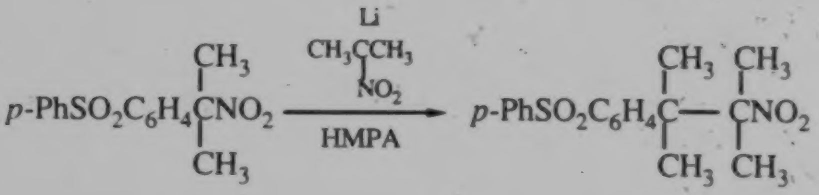
Along with 1,4-bis(2-nitropropyl)benzene, we also searched for other possible electron donors and acceptors which may be useful for the $S_{RN}1$ polymerization. The electron donor may polymerize with 1,4-bis(2,2-

dinitropropyl)benzene and the electron acceptor with the dilithium salt of 1,4-bis(2-nitropropyl)benzene.

One of the systems that we were interested in was the 4,4'-disubstituted diphenyl sulfone. Kornblum reported that 1-nitro-4-phenylsulfonylbenzene reacts with the lithium salt of 2-nitropropane in HMPA to give 4-phenylsulfonyl-α-nitrocumene[86] (equation 81). Even 4-phenylsulfonyl-α-nitrocumene can react with the lithium salt of 2-nitropropane (equation 82).[27]



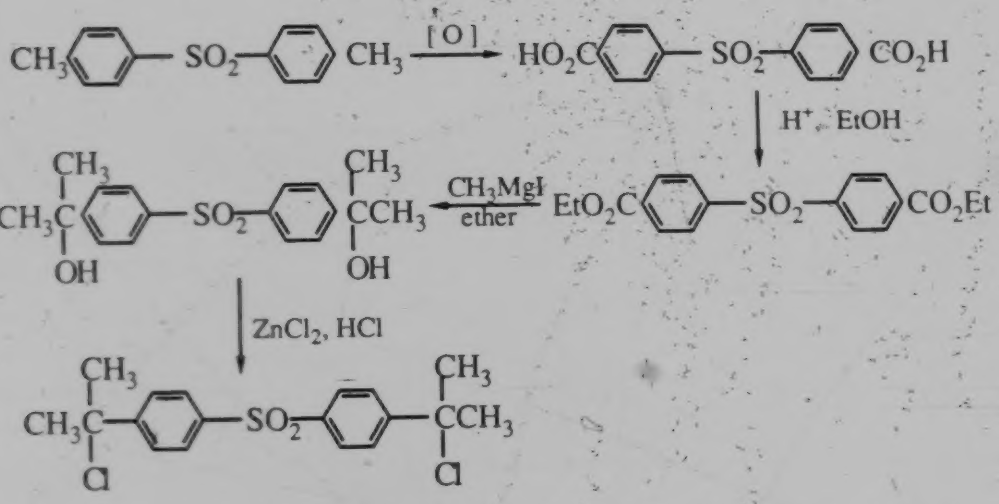
$$p\text{-}PhSO_2C_6H_4NO_2 \xrightarrow[\text{HMPA}]{\overset{\text{Li}}{CH_3\underset{NO_2}{C}CH_3}} p\text{-}PhSO_2C_6H_4\underset{CH_3}{\overset{CH_3}{C}}NO_2 \qquad (81)$$



$$p\text{-}PhSO_2C_6H_4\underset{CH_3}{\overset{CH_3}{C}}NO_2 \xrightarrow[\text{HMPA}]{\overset{\text{Li}}{CH_3\underset{NO_2}{C}CH_3}} p\text{-}PhSO_2C_6H_4\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}NO_2 \qquad (82)$$

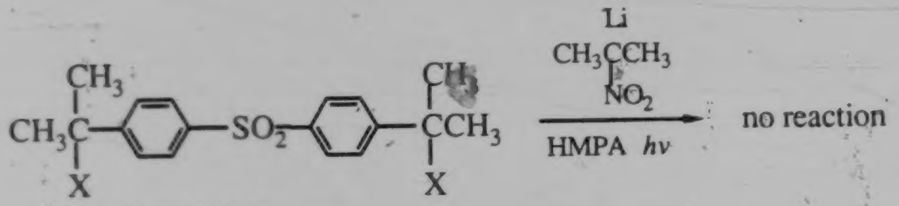
We thought that 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone may be a good electron acceptor for the polymerization.

The compound can be made from the corresponding alcohol. As shown in Scheme 28, the dicarboxylic acid was made by the oxidation of the sulfone and converted to the ester.[87,88] The alcohol can be made by the Grignard reaction. The conversion of the alcohol to the chloride was made by zinc chloride and conc. hydrochloric acid.[89] Attempts to purify the compound by flash chromatography remains unsuccessful because the elemental analysis



Scheme 28. Synthesis of 4,4'-bis[(1-chloro-1-methyl)ethyl]diphenyl sulfone.

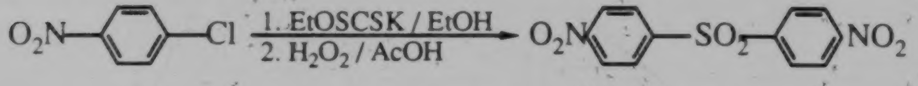
for chlorine was low. The NMR spectrum of the compound shows a singlet for the methyl protons at δ 1.95 ppm and multiplets for the aromatic protons at δ 7.65-8.00 ppm. The compound decomposes at 108° C. No reaction was observed for the reaction of the chloro compound (equation 83, X = Cl) with the lithium salt of 2-nitropropane. The starting material was recovered. The attempt to prepare 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone by the reaction of the chloride with sodium nitrite also failed.



X = Cl, NO$_2$.

(83)

4,4'-Dinitrodiphenylsulfone should be a good electron acceptor for the $S_{RN}1$ reaction because the mono-substituted compound 1-nitro-4-phenylsulfonylbenzene can react with lithium nitropropanate. The sulfone was made by the oxidation of 4,4'-dinitrodiphenyl sulfide (equation 84).[90] As



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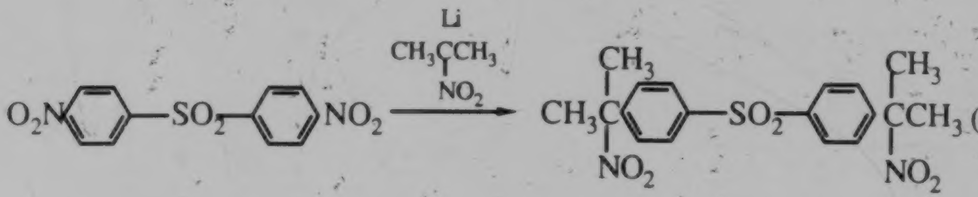
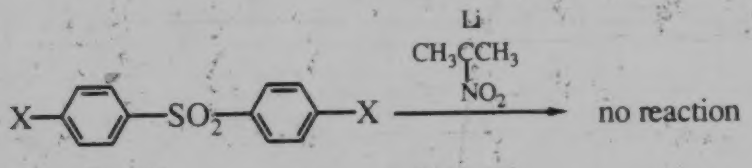


(85)

expected, the compound is quite reactive towards the lithium salt of 2-nitropropane (equation 85). The reaction is complete in 30 min. with illumination. The product 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone was isolated by precipitation with water and purified by recrystallization from ethanol. The yellow crystals decompose at 200° C. The NMR spectrum of the compound shows a singlet for the methyl protons at δ 2.00 ppm and two doublets for the aromatic protons at δ 7.63 and 8.05 ppm (J = 7 Hz).

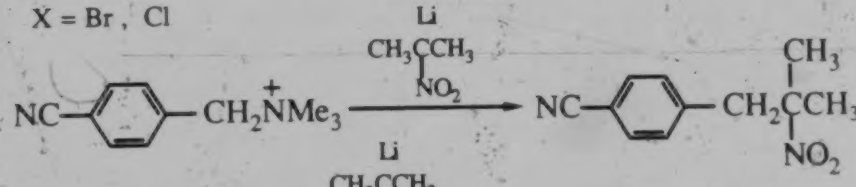
However, no product was obtained for the reaction of the product 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone with the lithium salt of 2-nitropropane. All the starting material was recovered even after the reaction was illuminated for 24 h. (equation 83, X = NO_2). Thus 4,4'-dinitrodiphenyl sulfone might be used for the polymerization but not 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone.

There is no reaction between *p*-dibromodiphenyl sulfone or *p*-dichlorodiphenyl sulfone and the lithium salt of 2-nitropropane (equation 86). The low reactivity of the compound may be attributed to the fact that chloro- and bromo-groups are not good electron acceptors for the reaction unlike the nitro group in 4,4'-dinitrodiphenyl sulfone. Thus the bromo and chloro compounds can not be used for polymerization.



(86)

X = Br , Cl



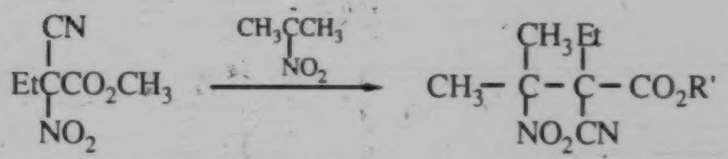
(87)

$$p\text{-}PhSO_2C_6H_4CH_2X \xrightarrow{\overset{\text{Li}}{\underset{NO_2}{CH_3CCH_3}}} \text{no reaction} \qquad (88)$$

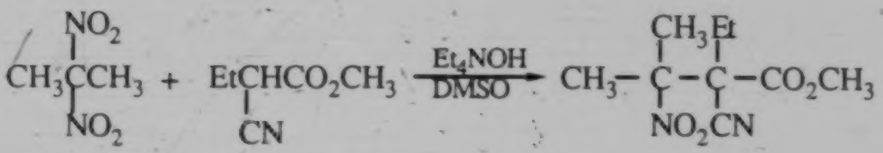
X = Br, NMe_3Br, NEt_3Br.

It was reported that the $S_{RN}1$ reaction can take place with *p*-cyanobenzyltrimethylammonium chloride but not with *p*-cyanobenzyl chloride (equation 87).[13] Thus, we considered that *p*-phenylsulfonylbenzyl systems may be good electron acceptors for the $S_{RN}1$ reaction. However, no product was isolated from the reaction of *p*-phenylsulfonylbenzyl bromide with the lithium salt of 2-nitropropane (equation 88, X = Br). Also no reaction was observed for the trimethylammonium or triethylammonium salt (X = NMe_3Br or NEt_3Br). The reaction of the dimethylsulfonium salt (X = SMe_3Br) with the lithium salt of 2-nitropropane produces an insoluble solid. No attempt was made to identify the insoluble material. These systems cannot be used for the polymerization.

An electron transfer reaction can occur at the carbon of 2-cyanoesters as shown in the reaction of 2-bromo-2-cyanoesters with nitrite ion. This can be further illustrated by the reaction of methyl 2-cyano-2-nitrobutanoate with the lithium salt of 2-nitropropane. The reaction produces the substituted product, methyl 2-cyano-2-ethyl-3-methyl-3-nitrobutanoate, in excellent yield (equation 89). The same product can be obtained in excellent yield by the



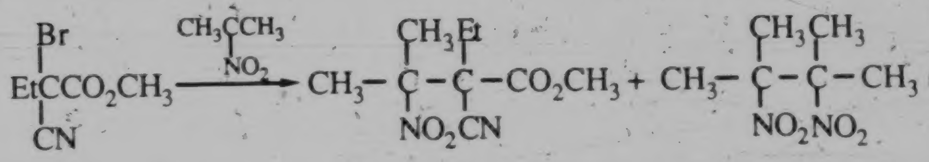
$$\mathrm{Et}\overset{\mathrm{CN}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{CO_2CH_3} \xrightarrow{\mathrm{CH_3\overset{}{\underset{\mathrm{NO_2}}{C}}CH_3}} \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}-\overset{\mathrm{Et}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{CO_2R'} \qquad (89)$$



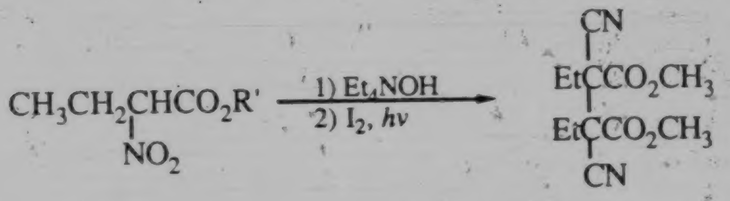
$$\mathrm{CH_3}\overset{\mathrm{NO_2}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{CH_3} + \mathrm{Et}\underset{\mathrm{CN}}{\mathrm{C}}\mathrm{HCO_2CH_3} \xrightarrow[\mathrm{DMSO}]{\mathrm{Et_4NOH}} \mathrm{CH_3}-\overset{\mathrm{CH_3}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}-\overset{\mathrm{Et}}{\underset{\mathrm{CN}}{\mathrm{C}}}-\mathrm{CO_2CH_3} \qquad (90)$$

reaction of the 2-cyanoester with 2,2-dinitropropane in the presence of tetraethylammonium hydroxide (equation 90). The compound was isolated by extraction and purified by dissolving in diethyl ether and precipitating at -70^0 C. It melts at 51^0 C. The NMR spectrum of the compound shows a singlet at δ 3.84 ppm for the methyl ester, a quartet of doublets at δ 2.16 ppm and a quartet of doublets at δ 1.86 ppm for the methylene protons (J = 7 and 14 Hz), two singlets at δ 1.84 and 1.88 ppm for the methyl protons, and a triplet at δ 1.13 ppm for the methyl protons of the ethyl group (J = 7 Hz).

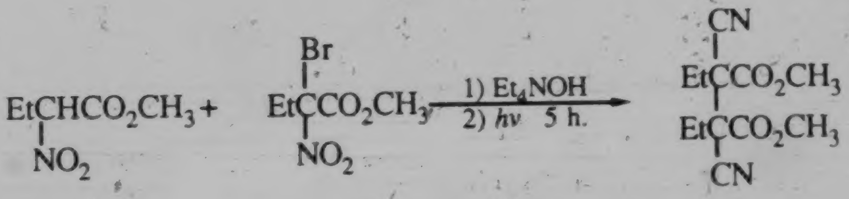
However, the 2-bromo-2-cyanoester is less reactive than the 2-cyano-2-nitroester. When methyl 2-bromo-2-cyanobutanoate is allowed to react with 2 equivalents of the tetraethylammonium salt of 2-nitropropane in DMSO, after illumination for 20 min, the product contains 2,3-dimethyl-2,3-dinitrobutane and methyl 2-cyano-2-ethyl-3-methyl-3-nitrobutanoate in a 1:3 ratio (equation 91) as determined from the NMR spectrum. Cross bromination occured in this case. The cross bromination product 2-bromo-2-nitropropane will react with the lithium salt of 2-nitropropane to produce 2,3-dimethyl-2,3-dinitrobutane.



$$\underset{\mathrm{CN}}{\overset{\mathrm{Br}}{\mathrm{EtCCO_2CH_3}}} \xrightarrow{\underset{\mathrm{NO_2}}{\mathrm{CH_3\overset{-}{C}CH_3}}} \mathrm{CH_3-}\underset{\mathrm{NO_2}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-}\underset{\mathrm{CN}}{\overset{\mathrm{Et}}{\mathrm{C}}}\mathrm{-CO_2CH_3} + \mathrm{CH_3-}\underset{\mathrm{NO_2}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-}\underset{\mathrm{NO_2}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{-CH_3} \qquad (91)$$



$$\underset{\mathrm{NO_2}}{\mathrm{CH_3CH_2CHCO_2R'}} \xrightarrow[\mathrm{2)\ I_2},\ h\nu]{\mathrm{1)\ Et_4NOH}} \begin{array}{c}\mathrm{CN}\\ \mathrm{EtCCO_2CH_3}\\ \mathrm{EtCCO_2CH_3}\\ \mathrm{CN}\end{array} \qquad (92)$$



$$\underset{\mathrm{NO_2}}{\mathrm{EtCHCO_2CH_3}} + \underset{\mathrm{NO_2}}{\overset{\mathrm{Br}}{\mathrm{EtCCO_2CH_3}}} \xrightarrow[\mathrm{2)}\ h\nu\ \mathrm{5\ h.}]{\mathrm{1)\ Et_4NOH}} \begin{array}{c}\mathrm{CN}\\ \mathrm{EtCCO_2CH_3}\\ \mathrm{EtCCO_2CH_3}\\ \mathrm{CN}\end{array} \qquad (93)$$

The anions of 2-cyanoesters can be used as electron donors. When the ammonium salt of the 2-cyanoester is allowed to react with iodine in the presence of light, the reaction only gives 32% yield of the dimer in 20 min.

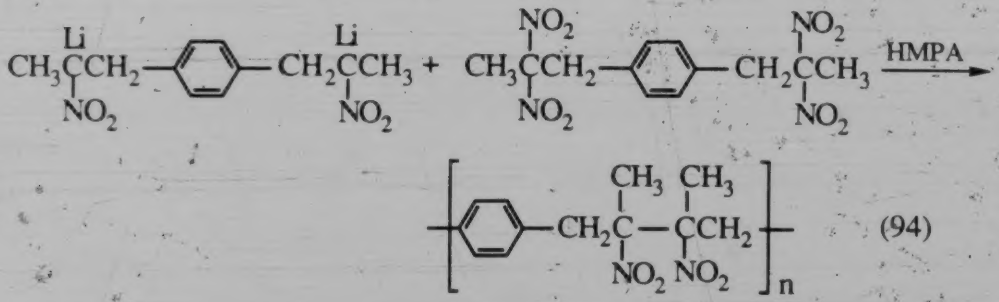
and only 60% in 7 h. (equation 92). The dimer can be also obtained in moderate yield by the reaction of the tetraethylammonium salt of the 2-cyanoester with the 2-bromo-2-cyanoester under illumination for 2 hours (equation 93). The dimer was isolated by the precipitation with water and purified by recrystallization from methanol. The crystals melt at 130-136^{0}C, and are a mixture of *dl* and *meso* isomers. The NMR spectrum of the dimer shows two singlets at 3.90 and 3.86 ppm for the methyl esters, and two multiplets at δ 1.88- 2.48 and 2.22-2.48 ppm for the methylene protons, and two triplets at δ 1.19 and 1.12 ppm for the methyl protons (J = 7 Hz). No product was isolated when the lithium salt of ethyl 2-cyanobutanoate reacted with ethyl 2-cyano-2-nitrobutanoate. Probably the nitroester was decomposed by the presence of water in the solvent. The reactivity of 2-cyanoesters is moderate. α,α'-Dicyanodiesters might be used for the polymerization.

IV. POLYMERIZATION

As discussed in the introduction, compounds that contain bifunctional groups (electron donor and acceptor) could be used for $S_{RN}1$ polymerization. We have mentioned in the last chapter that the polymerization of the dilithium salt of 1,4-bis(2-nitropropyl)benzene with 1,4-bis(2,2-dinitro-propyl)benzene only gave a trimer. In order to know why the polymerization fails, we made some efforts to investigate the $S_{RN}1$ reaction. From the study of the coupling reaction of the model compound, we realized that many factors influence the $S_{RN}1$ reaction. Disproportionation, solubility, ratio effect and reactivity are the four major factors. These factors should also influence the polymerization and should be solved before we can increase the molecular weight of the polymer. The most important factor seems to be the disproportionation which was never investigated before. We were able to increase the molecular weight for the $S_{RN}1$ polymerization of the 1,4-bis(2-nitropropyl)benzene system by decreasing the disproportionation. In the preliminary attempt, the reaction gave a polymer with average molecular weight of 5000 (after removal of nitro groups). We believe that the $S_{RN}1$ polymerization should be a new method to make a polymer.

Results and discussion

The synthesis of 1,4-bis(2-nitropropyl)benzene was mentioned in the third chapter. The dilithium salt of 1,4-bis(2-nitropropyl)benzene was used as an electron donor and 1,4-bis(2,2-dinitropropyl)benzene as an electron acceptor. HMPA was used as a solvent for the polymerization because the lithium salt is insoluble in DMSO and slightly soluble in HMPA. The reaction of the donor and acceptor (in 1:1 ratio) in HMPA produces a green colored mixture at the beginning which may be a charge transfer complex. The color

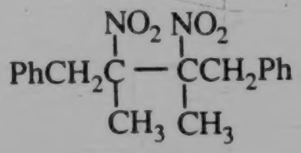


(94)

changes to yellow in half an hour. During the reaction, the lithium salt dissolves in three hours. After being stirred for 24 h. (equation 94), the product was easily isolated by precipitation with water. This product is soluble in chloroform and benzene. It was purified by dissoving in chloroform and precipitating with methanol. After the purification, the product is a light yellow solid. The average molecular (m.w.) weight is only 540 from the molecular weight analysis by the osmometric method in benzene.

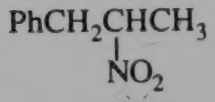
Many efforts were made to increase the molecular weight. At first, we tried the polymerization by increasing the reaction time. Since the $S_{RN}1$ reaction is a chain process, we believe that a longer reaction time should increase molecular weight for the polymerization if the polymerization is slow. However, the same reaction gave product with average molecular weight 750 after being stirred for 7 days. Even after 30 days, the average molecular weight was only increased to 840. It appears to be that the degree of polymerization does not depend on the reaction time. It is known that the $S_{RN}1$ reaction is always accelerated by light, so we tried the polymerization in the presence of a fluorescent light. The polymerization also gave a trimer (m.w. 830) after illumination for 48 h. From the above results, it seems that other effects influence the polymerization.

It is possible to estimate the molecular weight by measuring the integration ratio of the end group of the product and the C-C bond linkage in the NMR spectrum. The NMR spectrum shows many broad peaks which make analyzing the spectrum difficult. However, there are certain areas which can provide some valuable information about the structure of the end group of the product. We can distinguish the signal of the end group of the product and the C-C bond linkage by comparing the NMR spectrum of the dimer 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane and 2-nitro-1-phenylpropane. The



$$\mathrm{PhCH_2}\underset{\mathrm{CH_3}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}\mathrm{CH_2Ph}$$

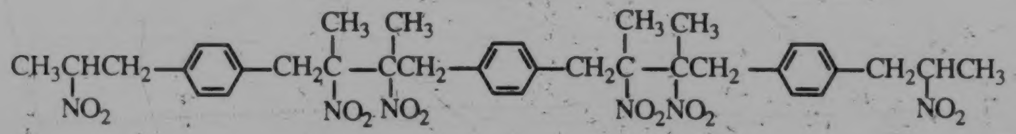
dl and *meso*



$$\mathrm{PhCH_2}\underset{\mathrm{NO_2}}{\mathrm{C}}\mathrm{HCH_3}$$

methylene protons of the dimer appear at δ 2.70, 3.08, 4.04 and 4.08 ppm as four doublets (J = 7 Hz) and the methyl protons appear at δ 1.38 and 1.58 ppm as two singlets. Because the product and the dimer have the same structure, the signals of the methyl and methylene protons should be located in the same region. The signal of the methylene protons of 2-nitro-1-

phenylpropane is located at δ 3.00 and 3.30 ppm as a doublet of doublets, that of the methyl protons at δ 1.58 ppm as a doublet (J = 7 Hz), and that of the methine proton at δ 4.77 ppm as a multiplet. These correspond to the structure of the end group. We can only use the signal of the methine proton at δ 4.8-5.2 ppm and the that of the methylene protons at δ 4.04 and 4.08 ppm to estimate the molecular weight. Because of the line broadening, other peaks may overlap with each other. The product, which was obtained by the reaction of the dilithium salt with the gem-dinitro compound under illumination for 48 h., shows an integration ratio about 1:4 between the methine proton (end group) and the methylene protons (the C-C bond linkage). If both end groups of the product are in the form $CH_3CH(NO_2)CH_2R$, then there should be 8 methylene protons in the product, which correspond to the trimer (m.w. 752). This estimated molecular weight is very close to that obtained by the osomometric method (m.w. 830).



The signals of the methyl and methylene protons of 2,2-dinitro-1-phenylpropane appear at δ 2.02 and 3.84 ppm. We did not observe these signals in the NMR spectrum of the product. This means that there is not this kind of the end group in the form of $CH_3C(NO_2)_2CH_2R$ in the product. Thus, 1,4-bis(2,2-dinitropropyl)benzene has been consumed completely for the reaction of the dilithium salt of 1,4-bis(2-nitropropyl)benzene with 1,4-

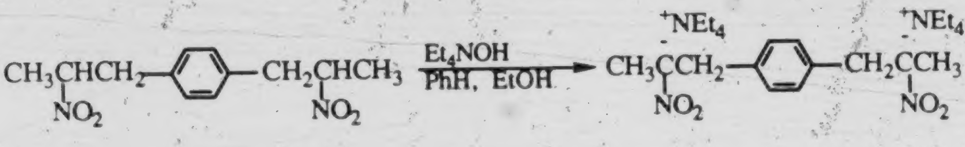
bis(2,2-dinitropropyl)benzene. Because a trimer was produced, the gem-dinitro groups must have reacted by another pathway.

From the above end group analysis, the disproportionation should be the major factor which should influence the polymerization. As discussed in the last chapter, the disproportionation reaction is one of the termination processes for the $S_{RN}1$ reaction. Once the termination reaction occurs, the chain process stops. We have shown that the reaction of the lithium salt of 2-nitro-1-phenylpropane (2 equivalents) with 2,2-dinitro-1-phenylpropane produces about 5% yield of disproportionation product. For the polymerization between the dilithium salt of 1,4-bis(2-nitropropyl)benzene and 1,4-bis(2,2-dinitropropyl)benzene, the disproportionation yield should be higher. It is useless to use excess dilithium salt of 1,4-bis(2-nitropropyl)benzene to prevent the disproportionation because the dilithium salt is only slightly soluble in HMPA.

The disproportionation reaction is the most important factor to be solved for the $S_{RN}1$ polymerization. Probably the disproportionation mainly results from the reaction of two radicals for the lithium nitronates. The disproportionation can be reduced by using a more reactive anion tetraethylammonium nitronate and by using iodine as a coupling reagent. In this case, the disproportionation was reduced to 2% when the ammonium salt of 2-nitro-1-phenylpropane and iodine were used in 2:1 ratio (molar ratio). The disproportionation yield was reduced further (in only 0.5% yield) when the ammonium salt and iodine were used in 3:1 ratio (molar ratio). Thus, polymerization should be possible by using the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene and iodine.

Solubility is the second problem which should be solved for the polymerization. Organolithium compounds are associated in dimeric, tetrameric or hexameric structures.[83] For the bifunctional compounds like the lithium salt of 1,4-bis(2-nitropropyl)benzene, the compounds should be polymeric and this is why the dilithium salt has a so low solubility in HMPA or DMSO.

We hoped that the tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene would be a more soluble salt. During the synthesis of the tetraethylammonium salt of 2-nitro-1-phenylpropane, we found that it is difficult to get a pure ammonium salt. The major problem is to remove water. The ammonium salt is fairly stable in the presence of water, but it decomposes very fast once water is removed. We found that it is possible to remove water by an azeotropic method. Because the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene is insoluble in benzene even in the presence of



(95)

water (equation 95), the conversion of 1,4-bis(2-nitropropyl)benzene to the ammonium salt by 20% Et_4NOH should be carried out in the presence of ethanol (benzene:95% ethanol = 3:1). The compound should be always protected by argon. After removal of water, the pure ammonium salt was obtained as a light yellow solid in 85% yield. The NMR spectrum shows three triplets for the methyl protons of the ethyl groups at δ 1.10-1.21 ppm (24 H), a singlet for the methyl protons at δ 2.74 ppm (6 H), a quartet for the methylene protons of the ethyl groups at δ 3.12 ppm (16 H), a singlet for the methylene protons at δ 3.62 ppm (4 H) and a singlet for the aromatic protons at δ 7.10 ppm (4 H). The ammonium salt is highly hygroscopic and decomposes slowly even under argon atomphere. The ammonium salt is still insoluble in HMPA and DMSO. Because the ammonium salt is very unstable, we found that it can be generated *in situ* in HMPA by using Et_4NOH solution as a base. Although the presence of water may reduce the reactivity of the ammonium salt because of the solvation effect, the effect may be small. Thus we can try the polymerization by using the ammonium salt in the presence of water (10-15%).

Based on the reaction of the model compound, we found another problem, that is, the ratio effect. As discussed in the last chapter, for the reaction of 2-nitro-1-phenylpropane with 2,2-dinitro-1-phenylpropane, when in a 1:1 molar ratio, proceeds to 75% completion in 20 min. with illumination and only 80% after 5 hours. Because the reaction cannot go to completion, it is impossible for the reaction of the dilithium salt of 1,4-bis(2-nitropropyl)benzene and 1,4-bis(2,2-dinitropropyl)benzene to give a polymer with high molecular weight. The ratio effect should be another factor which influences the polymerization of the dilithium salt of 1,4-bis(2-nitropropyl)benzene and 1,4-bis(2,2-dinitropropyl)benzene. This effect only occurs when the lithium nitronate and the gem-dinitro compound are used for

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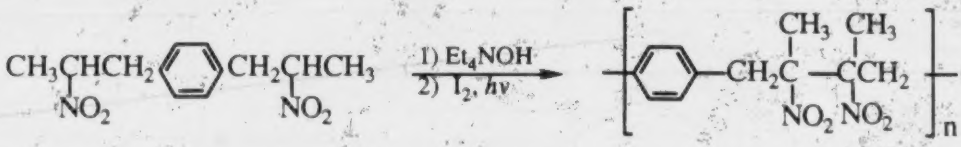
the $S_{RN}1$ reaction. The effect is unimportant for the reaction of the tetraethylammonium salt of 2-nitro-1-phenylpropane with iodine in HMPA.

We also found that the reactivity of the lithium salt of 2-nitro-1-phenylpropane is lower than the ammonium salt. The slow formation of the C-C bond results in longer reaction time for polymerization. This low reactivity may also increase the disproportionation. However, in the presence of light, the difference of the reactivity becomes smaller.

The $S_{RN}1$ reaction can be accelerated by light. The presence of light can even cause the elimination of the vicinal nitro groups by lithium nitronates. We found that it is impossible by illumination to increase the molecular weight for the reaction of the dilithium salt of 1,4-bis(2-nitropropyl)benzene with 1,4-bis(2-nitropropyl)benzene.

From the above discussion, we know why the polymerization of the dilithium salt with the gem-dinitro compound fails. From the study of the coupling reaction of the model compound, we discovered that the carbon carbon bond formation can be achieved by using tetraethylammonium nitronates and iodine. Higher reactivity was observed for the reaction in acetonitrile than in HMPA. We tried the polymerization in CH_3CN, but a precipitate formed immediately when iodine was added the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene solution. HMPA or DMSO was used for the polymerization because the polymer is more soluble in these solvents.

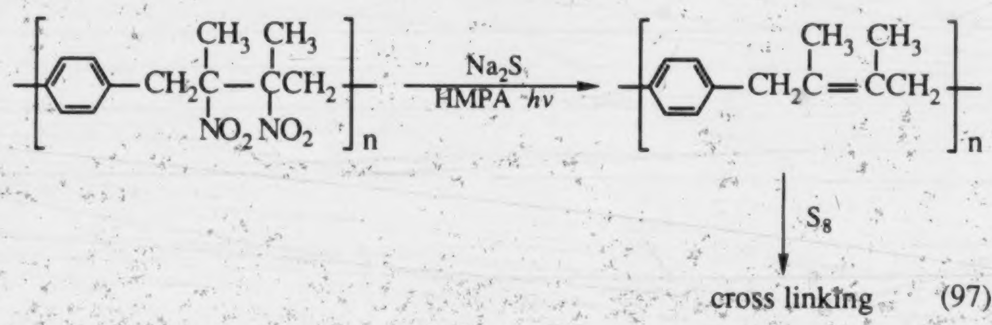
We were successful in obtaining the polymer by using the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene as an electron donor (equation 96), which was generated by the reaction of 1,4-bis(2-nitropropyl)benzene with an equivalent of Et_4NOH solution, and iodine as a coupling reagent (in 2:1 molar ratio). HMPA or DMSO was used as a solvent for the polymerization. The polymerization in both solvents gave the same



CH3CHCH2
NO2
CH2CHCH3
NO2
1) Et4NOH
2) I2, hv
CH3 CH3
CH2C — CCH2
NO2 NO2
n

(96)

result. After illumination for 24 h. under argon, the polymer was isolated by precipitation with water. The polymer is slightly soluble in HMPA, but insoluble in DMSO. The low solubility makes the characterization of the polymer impossible. To make a soluble polymer, the nitro groups in the polymer were eliminated by sodium sulfide. The elimination takes about 48 h. in HMPA with illumination, but it is very slow in DMSO. The elimination polymer should have the structure shown (equation 97). This polymer is

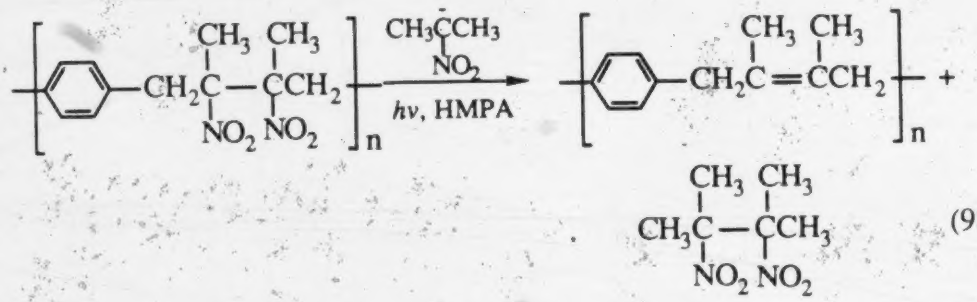


CH3 CH3
CH2C — CCH2
NO2 NO2
n
Na2S
HMPA hv
CH3 CH3
CH2C = CCH2
n
S8
cross linking

(97)

soluble in chloroform, but it contains sulfur as indicated from the mass spectrum. The polymer was purified by dissolving in chloroform and subsequently precipitating with methanol, but became an insoluble solid after drying at 80^0 C under vacuum. We realized later that the presence of sulfur can cause the cross linking to the polymer. Because sulfur is present in the polymer, the cross linking should happen at elevated temperature (equation 97), which should make the polymer insoluble. Thus an alternative reduction method has to be used.

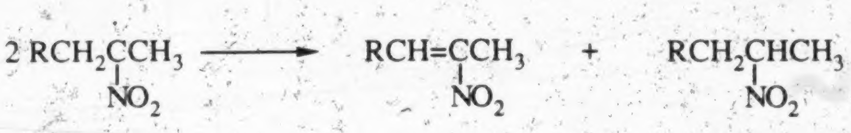
As mentioned in the last chapter, the lithium salt of 2-nitropropane can promote the elimination of nitro groups from the dimer, 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane. It should be possible to eliminate vicinal nitro groups by using excess of the lithium salt of 2-nitropropane. In this way, we can avoid introducing sulfur into the polymer. The reaction was carried out in HMPA because the polymer is only slightly soluble in this solvent (equation 98). The reaction is very slow. After illumination for 7 days, the polymer dissolved. The elimination polymer was isolated by precipitation with water. Although the reaction will produce 2,3-dimethyl-2,3-dinitrobutane as a by-product, it is relatively easy to remove the by-product by extraction with methanol because the polymer is only slightly soluble in boiling methanol. The polymer was further purified by extraction with ethyl acetate. The



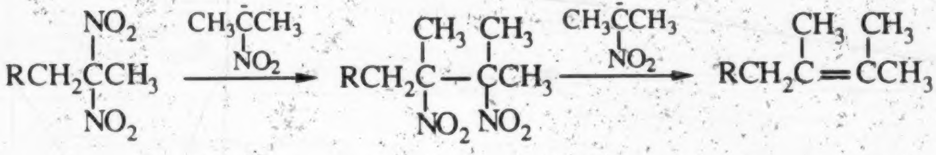
(98)

weight of the elimination polymer obtained was measured by the osmometric method in dibromomethane solution. The average molecular weight of the polymer is 4888.

The NMR spectrum of the polymer only shows two broad peaks at δ 1.68 and 1.74 ppm for the methyl protons, two broad peaks at δ 3.26 and 3.52 ppm for the methylene protons, and a broad peak at δ 7.10 ppm for the aromatic protons. No signal of the end group could be observed. Probably the signal is too weak to be observed. We do not know whether the end group is in the form of $CH_3CH(NO_2)CH_2R$ or $Me_2C{=}C(Me)CH_2R$. The former end group should result from the disproportionation (equation 99). The latter one



$$2\,RCH_2\underset{NO_2}{C}CH_3 \longrightarrow RCH{=}\underset{NO_2}{C}CH_3 + RCH_2\underset{NO_2}{C}HCH_3 \qquad (99)$$



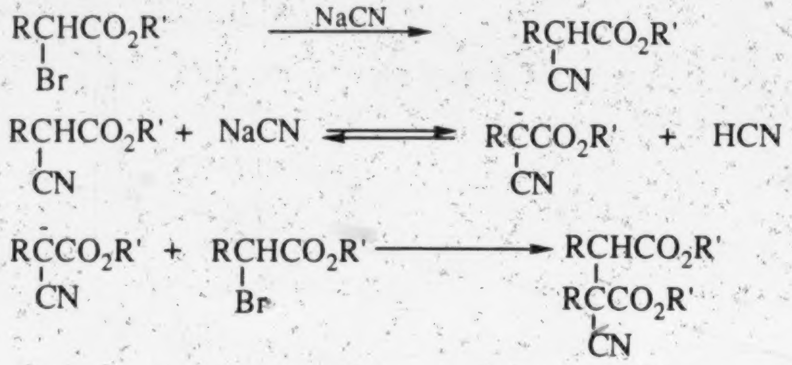
$$RCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_3 \xrightarrow{\underset{NO_2}{CH_3\bar{C}CH_3}} RCH_2\underset{NO_2}{\overset{CH_3}{C}}-\underset{NO_2}{\overset{CH_3}{C}}CH_3 \xrightarrow{\underset{NO_2}{CH_3\bar{C}CH_3}} RCH_2\overset{CH_3}{C}{=}\overset{CH_3}{C}CH_3 \qquad (100)$$

should be from the reaction of the gem-dinitro groups with the lithium salt of 2-nitropropane (equation 100) and subsequently elimination of the vicinal nitro groups. From the IR spectrum, very strong absorptions at 1547 and 1508 cm^{-1} were observed, which are probably from the end group $CH_3CH(NO_2)CH_2R$.

Although the molecular weight is not high for the $S_{RN}1$ polymerization, it is possible to increase the molecular weight by using a better solvent or more soluble ammonium nitronates for the polymerization. Because the ditetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene is only slightly soluble in dipolar aprotic solvents like DMSO and HMPA, we could only try the polymerization in the presence of water (10%). The presence of water should have some solvation effect although the magnitude is not known. The solubility of the ammonium salt may be increased by using the tetrabutylammonium salt. This remains to be investigated.

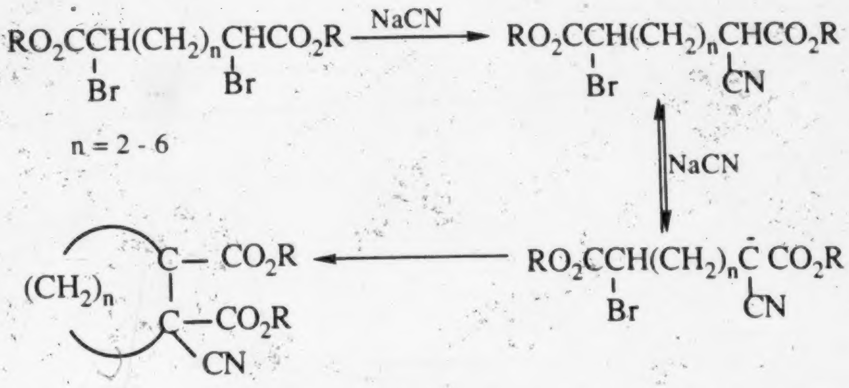
V. FRANCHIMONT REACTION

The Franchimont reaction[69] is the dimerization reaction of 2-bromoesters with sodium cyanide to form a substituted succinate diester. The reaction is illustrated in Scheme 29. As mentioned in the second chapter, the pKa values of hydrogen cyanide and 2-cyanoesters are almost the same (about 8-9). Because sodium cyanide is only slightly soluble in methanol or in DMSO (the solubility of sodium cyanide in methanol is only 6.8% by weight at 15° C),[91a] the concentration of cyanide ion is low. The competition between the anion of 2-cyanoesters and cyanide ion results in the formation of the succinate diester. Actually, this reaction is very useful for the synthesis of alkylated succinate diesters or succinic acids.[91b]



Scheme 29. The Franchimont reaction mechanism.

In the case of 2,5-, 2,6- and 2,7-dibromodiesters, the reaction of the α,α'-dibromodiesters with cyanide ion produces four, five and six-membered rings respectively.[92-95] As shown in Scheme 30, the cyclization is basically



Scheme 30. The reaction mechanism of α,α'-dibromodiesters with sodium cyanide.

the same as the dimerization. The reaction of α,α'-dibromodiesters with cyanide ion produces mono-substitutited products α-bromo-α'-cyanodiesters first, and then the α-bromo-α'-cyanodiesters cyclize to form 4-6 membered rings immediately after the deprotonation of the mono-substituted product. The cyclizations for a small ring (n ≤ 4) are intramolecular reactions and should be much faster than the dimerization because the effective concentration of the internal nucleophile is always high. On the other hand, no cyclization was reported for the formation of a seven membered ring (n = 5) because the cyclization is slow.[95]

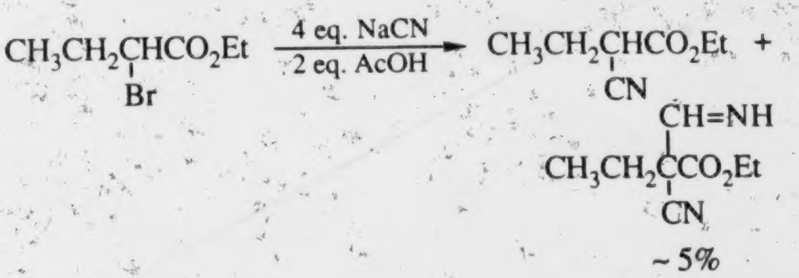
During the synthesis of ethyl 2-cyanopropanoate, we found two methods which can inhibit the dimerization for the reaction of 2-bromoesters with cyanide ion. The first method is by using a buffer for the substitution and the second one by using tetraethylammonium cyanide to increase the concentration of the cyanide ion. In order to know whether these two methods are useful for the synthesis of α,α'-dicyanodiesters by the reaction of α,α'-

dibromodiesters with cyanide ion, we studied the Franchimont reaction. Although the dimerization can be inhibited by using the above two methods, efforts to prevent the cyclization still remain unsuccessful probably because the cyclization is a very fast process. We will discuss the inhibition of the dimerization for the reaction of 2-bromoesters with cyanide ion and the attempted synthesis of α,α'-dicyanodiesters separately.

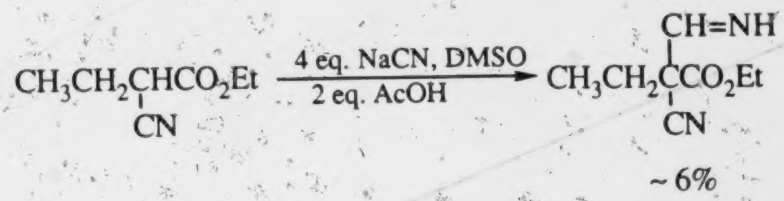
Results and Discussion

1. The inhibition of the dimerization reaction of 2-bromoesters with NaCN

As mentioned above, because of the competition between the anion of 2-cyanoesters and cyanide ion, the reaction of 2-bromoesters with cyanide ion in alcohol gives 2-cyanoesters in 20% yield.[69] We hoped that DMSO would be a better solvent for the substitution. The dipolar aprotic solvent usually accelerates the substitution because the nucleophilicity of cyanide ion can be increased. However, the reaction of ethyl 2-bromopropanoate with sodium cyanide in DMSO gives ethyl 2-cyanopropanoate in only 40% yield. Because the succinate results from the competition between the anion of 2-cyanoesters and cyanide ion, it should be possible to increase the yield of 2-cyanoesters by increasing the concentration of cyanide ion or by inhibiting the deprotonation of 2-cyanoesters. As mentioned earlier, the concentration of cyanide ion cannot be increased by using excess sodium cyanide because the solubility is limited. However, it is possible to prevent the deprotonation of 2-cyanoesters by cyanide ion with a buffer. Therefore, the dimerization can be sufficiently inhibited without affecting the substitution. Indeed, a good yield was obtained when two equivalents of acetic acid and four equivalents sodium cyanide were stirred with ethyl 2-bromobutanoate for 5 h. (equation 101). In addition, the



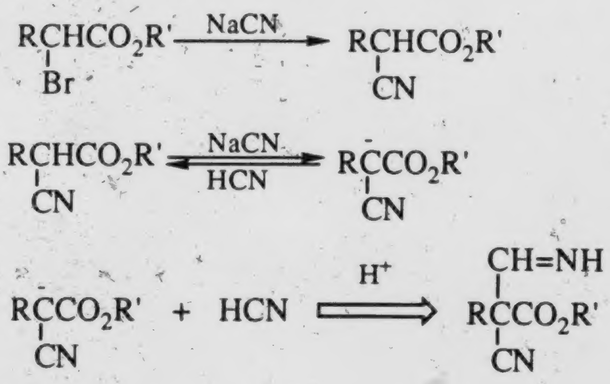
$$\underset{Br}{CH_3CH_2CHCO_2Et} \xrightarrow[\text{2 eq. AcOH}]{\text{4 eq. NaCN}} \underset{CN}{CH_3CH_2CHCO_2Et} + \underset{\sim 5\%}{\overset{CH=NH}{\underset{CN}{CH_3CH_2CCO_2Et}}} \qquad (101)$$



$$\underset{CN}{CH_3CH_2CHCO_2Et} \xrightarrow[\text{2 eq. AcOH}]{\text{4 eq. NaCN, DMSO}} \underset{\sim 6\%}{\overset{CH=NH}{\underset{CN}{CH_3CH_2CCO_2Et}}} \qquad (102)$$

major by-product was ethyl 2-cyano-2-ethyl-3-iminopropanoate in about 5% yield. The iminoester was also obtained in 6% yield in a control experiment when the 2-cyanoester was stirred with the same buffer (HCN-NaCN) for two days (equation 102). Ethyl 2-cyano-2-ethyl-3-iminopropanoate was purified by distillation under vacuum. It is a white crystalline material, mp $113-114^0$ C. It shows a broad NMR signal for both protons of the imino group at δ 5.38-6.38 ppm and an absorption at 1556 cm^{-1} in the IR spectrum for the C=N bond. The stability of the compound is probably because the imino-group is attached to the tertiary carbon. Because of the steric hindrance, the hydrolysis of the imine should be much slower than that of a normal imine.

The formation of the iminoester is a good indication of the reaction mechanism as shown in Scheme 31. The presence of the buffer prevents the deprotonation of the product 2-cyanoester by cyanide ion and thus reduces the competition with cyanide ion. After the substitution is complete (there is no more 2-bromoester), the presence of a small amount of the anion reacts with HCN to form the iminoester, but only a low yield was obtained.

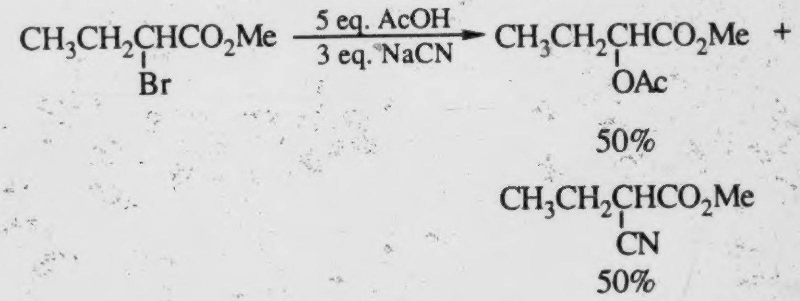


Scheme 31. The formation of the iminoester.

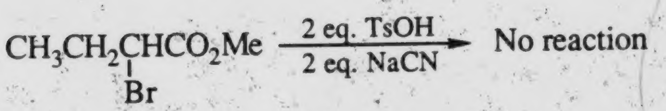
We also tried different solvents for the reaction in the presence of the buffer solution. DMSO is the best solvent because the substitution reaction is complete in 5 h. as observed by TLC. Thus DMSO was used for most substitution reactions. When the same reaction is carried out in methanol, although no dimerization reaction occurs, the reaction is only 60% complete in 18 h. and only 80% in 52 h. as determined from the NMR spectrum.

When acetic acid was used as an acid to form a buffer (HCN-NaCN) for the reaction of dimethyl 2,5-dibromoadipate with sodium cyanide, the dimerization still occured. Thus, other possible buffer systems were investigated. These buffer systems were also tried first in order to know whether they are useful to inhibit the dimerization of 2-bromoesters.

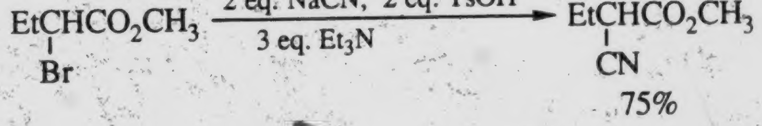
Apparently, acetic acid cannot be used in excess because the reaction of methyl 2-bromobutanoate with sodium cyanide (three equivalents) in the presence of acetic acid (five equivalents) gave two products in about 1:1 ratio. From the NMR spectrum, one of them is methyl 2-cyanobutanoate and the other is probably methyl 2-acetoxybutanoate (equation 103), which results from the substitution by acetate ion. The compound shows a triplet for the methine proton at δ 4.98 ppm, a singlet for the methyl ester protons at δ 3.78 ppm, a singlet for the methyl protons of acetyl group at δ 2.15 ppm and a triplet for the methyl protons of the ethyl group at δ 1.00 ppm (the signal of the methylene protons is overlapped with those of methyl 2-cyanobutanoate).



$$CH_3CH_2\underset{Br}{C}HCO_2Me \xrightarrow[3\text{ eq. NaCN}]{5\text{ eq. AcOH}} \underset{50\%}{CH_3CH_2\underset{OAc}{C}HCO_2Me} + \underset{50\%}{CH_3CH_2\underset{CN}{C}HCO_2Me} \quad (103)$$



$$CH_3CH_2\underset{Br}{C}HCO_2Me \xrightarrow[2\text{ eq. NaCN}]{2\text{ eq. TsOH}} \text{No reaction} \quad (104)$$



$$Et\underset{Br}{C}HCO_2CH_3 \xrightarrow[3\text{ eq. }Et_3N]{2\text{ eq. NaCN, 2 eq. TsOH}} \underset{75\%}{Et\underset{CN}{C}HCO_2CH_3} \quad (105)$$

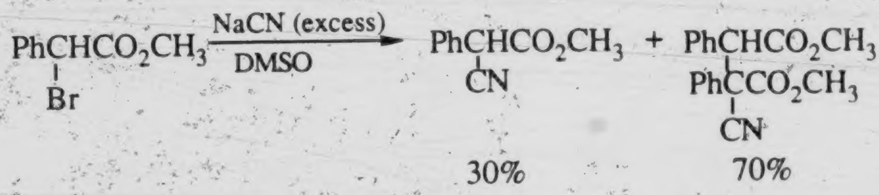
To avoid the substitution by acetate ion, *p*-toluenesulfonic acid was used. However, no reaction occured when *p*-toluenesulfonic acid and sodium cyanide were used both in two equivalents (equation 104). The presence of an amine is necessary to deprotonate HCN when the acid and cyanide ion are used in 1:1 ratio. The reaction of methyl 2-bromobutanoate with sodium cyanide (two equivalents) in the buffer (TsOH:Et_3N = 2:3) produces 75% yield of methyl 2-cyanobutanoate (equation 105). This method may serve as an alternative way for the synthesis of 2-cyanoesters by the substitution (tertiary amines should be used because a secondary amine will react with 2-bromoesters to form stable 2-dialkylaminoester products).

Other buffer systems comprised of *p*-toluenesulfonic acid and amines such as N,N-dimethylaniline, benzyldimethylamine or N-methylmorpholine were also studied. Although no dimerization occurs, the substitution is slow when methyl 2-bromoesters are allowed to react with sodium cyanide (three equivalents) in the buffer (TsOH:Amine = 3:3). However, even in these buffer systems, the cyclization reaction of dimethyl 2,5-dibromoadipate with cyanide ion still takes place. Probably it is difficult to prevent the cyclization by using a buffer solution because we found later that the cyclization is a very fast process. Thus the reaction of methyl α-bromophenylacetate with cyanide was studied because the substitution may proceed faster.[96a] From a study of the reaction of methyl α-bromophenylacetate with cyanide ion, we hoped to find a better system which can be used to inhibit the cyclization of α,α'-dibromodiesters.

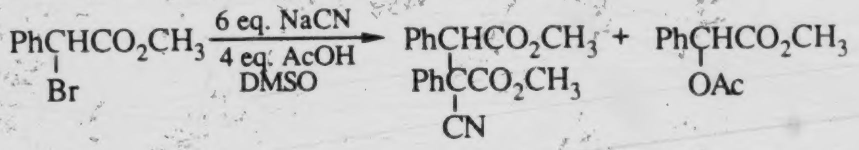
2. The inhibition of the dimerization reaction of methyl α-cyanophenylacetate with cyanide ion

Because of the presence of the phenyl group, the substitution between methyl α-bromophenylacetate and cyanide ion, and the dimerization between the α-bromoacetate and the product methyl α-cyanophenylacetate should proceed faster. The substitution product methyl α-cyanophenylacetate should be more acidic than 2-cyanoesters. The validity of the buffer systems were tested by the reaction of methyl α-bromophenylacetate with cyanide ion.

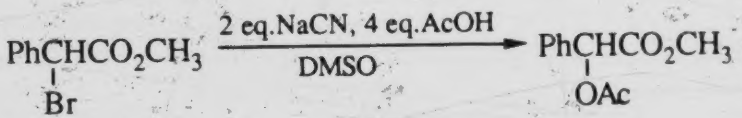
The reaction of methyl α-bromophenylacetate with sodium cyanide in alcohol gives the dimer dimethyl 2-cyano-2,3-diphenylsuccinate as a major product.[69] We also tried the reaction in DMSO and obtained the same result (equation 106). When acetic acid (4 equivalents) and sodium cyanide (6 equivalents) were used, the dimerization still took place, but the by-product



$$\underset{\text{Br}}{\mathrm{PhCHCO_2CH_3}} \xrightarrow[\text{DMSO}]{\text{NaCN (excess)}} \underset{\substack{\text{CN}\\ \\ 30\%}}{\mathrm{PhCHCO_2CH_3}} + \begin{array}{c}\mathrm{PhCHCO_2CH_3}\\ |\\ \mathrm{PhCCO_2CH_3}\\ |\\ \mathrm{CN}\\ \\ 70\%\end{array} \tag{106}$$



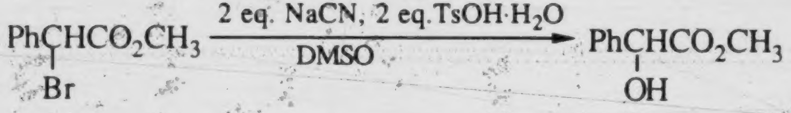
$$\underset{\text{Br}}{\mathrm{PhCHCO_2CH_3}} \xrightarrow[\substack{\text{4 eq. AcOH}\\ \text{DMSO}}]{\text{6 eq. NaCN}} \begin{array}{c}\mathrm{PhCHCO_2CH_3}\\ |\\ \mathrm{PhCCO_2CH_3}\\ |\\ \mathrm{CN}\end{array} + \underset{\text{OAc}}{\mathrm{PhCHCO_2CH_3}} \tag{107}$$



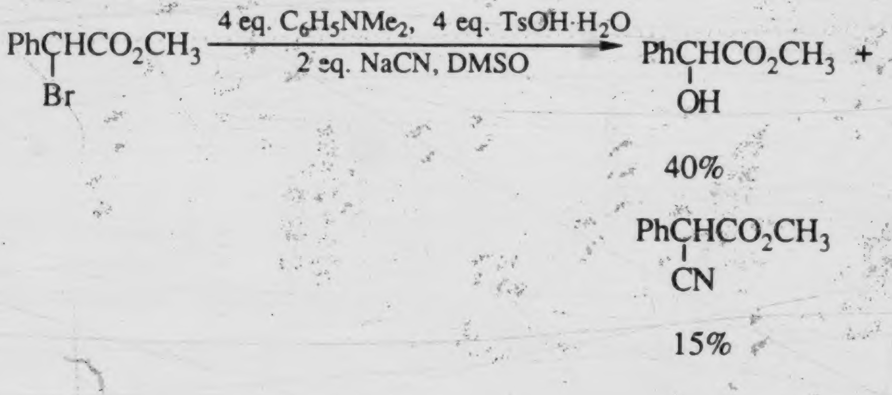
$$\underset{\text{Br}}{\mathrm{PhCHCO_2CH_3}} \xrightarrow[\text{DMSO}]{\text{2 eq.NaCN, 4 eq.AcOH}} \underset{\text{OAc}}{\mathrm{PhCHCO_2CH_3}} \tag{108}$$

was methyl α-acetoxyphenylacetate (equation 107). When acetic acid (4 equivalents) and NaCN (2 equivalents) were used, there was no cyanide ion in the solution and only methyl α-acetoxyphenylacetate was obtained (equation 108). Acetate anion is a good nucleophile and thus substitution by acetate ion should take place. The product methyl α-acetoxyphenylacetate was identified by the NMR spectrum, which shows a singlet for the methine proton at δ 5.93 ppm, a singlet for the methyl protons of the ester at δ 3.70 ppm and a singlet for the methyl protons of the acetyl group at δ 2.18 ppm. No attempt was made to isolate the product and measure the yield.

Therefore, *p*-toluenesulfonic acid was used because its sodium salt is a weak nucleophile. Instead of obtaining the 2-cyanoester, methyl α-hydroxyphenylacetate was obtained when the acid and sodium cyanide (both two equivalents) were used (equation 109). The product was identified by the NMR spectrum, which is identical to that reported in the literature.[121] The



$$\underset{\text{Br}}{\text{PhCHCO}_2\text{CH}_3} \xrightarrow[\text{DMSO}]{\text{2 eq. NaCN, 2 eq.TsOH}\cdot\text{H}_2\text{O}} \underset{\text{OH}}{\text{PhCHCO}_2\text{CH}_3} \qquad (109)$$

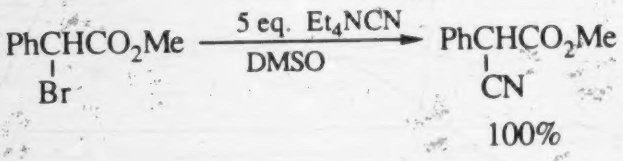


$$\underset{\text{Br}}{\text{PhCHCO}_2\text{CH}_3} \xrightarrow[\text{2 eq. NaCN, DMSO}]{\text{4 eq. C}_6\text{H}_5\text{NMe}_2\text{, 4 eq. TsOH}\cdot\text{H}_2\text{O}} \underset{\substack{\text{OH}\\ 40\%}}{\text{PhCHCO}_2\text{CH}_3} + \underset{\substack{\text{CN}\\ 15\%}}{\text{PhCHCO}_2\text{CH}_3} \qquad (110)$$

formation of methyl α-hydroxyphenylacetate is slow and takes 4 days. It seems that the substitution results from the presence of water ($TsOH{\cdot}H_2O$ is used).

Other buffer systems are not satisfactory for the reaction. When N,N-dimethylaniline and *p*-toluenesulfonic acid (4 equivalents each) were used as a buffer, the reaction of methyl α-bromophenylacetate with NaCN (three equivalents) still produced the 2-hydroxyester (equation 110). The reaction in the buffer system of N-methylmorpholine and *p*-toluenesulfonic acid gave the same result. From the above results, the buffer systems have no effect for the substitution reaction. The reaction may only depend on the concentration of the nucleophile because methyl α-bromophenylacetate is so reactive that the normal buffer system is no longer useful to prevent the dimerization.

Methyl α-cyanophenylacetate should be more acidic than 2-cyanoesters. Therefore, it may be impossible to prevent the deprotonation of α-cyanophenylacetate by cyanide ion in a normal buffer system. Because methyl α-bromophenylacetate is very reactive, it may be possible to control the substitution by increasing the concentration of the cyanide ion. Thus a more soluble cyanide reagent should be used. Tetraethylammonium cyanide was used because we found that it is very soluble in DMSO. In fact, the reaction of methyl α-bromophenylacetate with Et_4NCN (5 equivalents) in DMSO gave



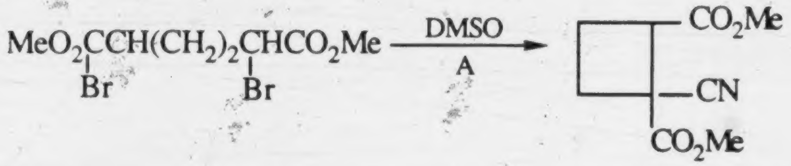
$$\underset{\displaystyle Br}{PhCHCO_2Me} \xrightarrow[\text{DMSO}]{\text{5 eq. } Et_4NCN} \underset{\displaystyle \underset{100\%}{CN}}{PhCHCO_2Me} \qquad (111)$$

methyl α-cyanophenylacetate in quantitative yield (equation 111). The product shows an NMR spectrum identical to that in the literature.[122] The reaction may be complete in 5 min., but no attempt was made to monitor the reaction. The dimerization is eliminated in this case probably due to the high reactivity of the bromoester and high concentration of cyanide ion.

3. The attempted synthesis of dimethyl 2,5-dicyanoadipate

The reaction of diethyl 2,5-dibromoadipate with sodium cyanide in 40% DMSO at 80° C was reported to give diethyl 2,5-dicyanoadipate.[96b] We repeated the reaction several times using dimethyl 2,5-dibromoadipate, but only cyclized dimethyl 1-cyanocyclobutane-1,2-dicarboxylate was obtained.

The reaction of dimethyl 2,5-dibromoadipate with sodium cyanide in methanol gave the cyclized product.[93b] We also obtained the same result for the reaction in DMSO (equation 112). The *cis*- and *trans*- isomers of the cyclobutane can be separated by recrystallization from methanol.[93b] One of the isomers (solid) shows the methyl protons at δ 3.72 and 3.85 ppm and the other (liquid) at δ 3.80 and 3.89 ppm.

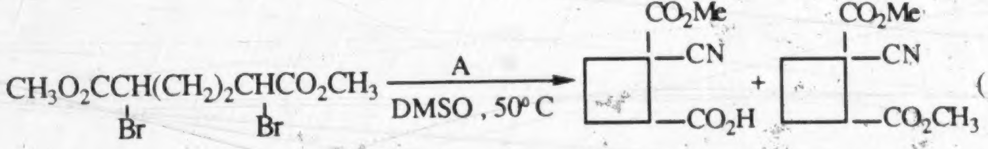


(112)

	yield
A = NaCN	73%
NaCN : AcOH = 9 : 4	65%

As discussed above, we have two methods to inhibit the dimerization for the reaction of 2-bromoesters with cyanide ion. We wished to extend the application for the synthesis of α,α'-dicyanodiesters by the reaction of α,α'-dibromodiesters with cyanide ion.

The substitution in the buffer system was tried first. However, the reaction of dimethyl 2,5-dibromoadipate with sodium cyanide (9 equivalents) in the presence of acetic acid (3 equivalents) in DMSO only formed the cyclized product, dimethyl 1-cyanocyclobutane-1,2-dicarboxylate, in 65% yield (equation 113). No α,α'-dicyanoadipate was formed because we could not find any signal of the methine proton of the 2-cyanoester at δ 3.6 ppm in the NMR spectrum. When sodium cyanide and acetic acid (in 1:1 ratio) were used, no reaction took place. The reaction of dimethyl 2,5-dibromoadipate with sodium cyanide (2 equivalents) in other buffer systems such as N-methylmorpholine and *p*-toluenesulfonic acid (in a 3:3 ratio) still formed the cyclized product.



$$CH_3O_2CCH(Br)(CH_2)_2CH(Br)CO_2CH_3 \xrightarrow[\text{DMSO, } 50^{\circ}C]{A} \qquad (113)$$

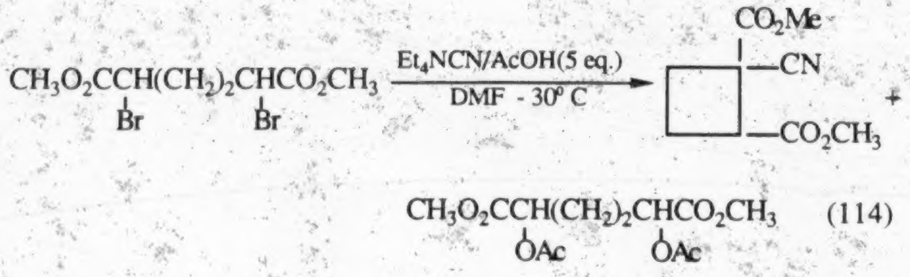
A =	ratio		
(a) 8 eq. Et_4NCN	1	:	0
(b) 4 eq. Et_4NCN	1	:	1
(c) 7 eq. Et_4NCN 1 eq. AcOH	1	:	1

We also tried to use Et_4NCN for the substitution. The saturated solution of tetraethylammonium cyanide in DMSO is about 3.2 N at 50°C. The concentration of 2,5-dibromoadipate was controlled to be as low as 0.4 N (0.2 mol). When the reaction was stirred at 50° C overnight, we isolated a mixture, which is probably the *trans* and *cis* isomers of mono-hydrolyzed carboxylic acid 2-cyano-2-methoxycarbonylcyclobutane-carboxylic acid because the compound shows a strong absorption in the IR between 2800-3200 cm^{-1} (equation 113). We found later that the reaction of 2,7-dibromosuberate with Et_4NCN at 50° C in DMSO also gave a mono-hydrolyzed carboxylic acid under the same reaction condition. The NMR spectrum of the mixture shows two singlets for the protons of the methyl groups at δ 3.75 and 3.83 ppm. The signals are different from those of dimethyl 1-cyanocyclobutane-1,2-dicarboxylate (the protons of the methyl groups for the solid isomer dimethyl 1-cyanocyclobutane-1,2-dicarboxylate appear at δ 3.72 and 3.85 ppm and those for the liquid isomer at δ 3.80 and 3.89 ppm). However, no hydrolysis was observed if the reaction mixture was stirred at room temperature for 24 hours.

When a lower concentration of tetraethylammonium cyanide (1.60 N) was used and the reaction mixture was stirred at 50° C for 20 h., several products were obtained (equation 113). Six singlets for the protons of methyl groups at δ 3.73, 3.75, 3.80, 3.83, 3.86 and 3.89 ppm were observed in the NMR spectrum. These peaks belong to the *cis* and *trans* dimethyl 1-cyanocyclobutane-1,2-dicarboxylates and their mono-hydrolyzed products *cis* and *trans* 2-cyano-2-methoxycarbonylcyclobutane-carboxylic acids. No absorption for the methine proton of the 2-cyanoester $RCH(CN)CO_2R'$ could be observed. It seems that the hydrolysis should take place in the secondary ester group because this ester group is less hindered. The hydrolysis of esters catalyzed by nucleophiles (e.g. LiI or RS^-) is known and many examples have been reported.[97]

From the above results, it appears that it is impossible to inhibit the cyclization of dimethyl 2,5-dibromoadipate by using the buffer conditions or tetraethylammonium cyanide. At last, we tried the reaction by using Et_4NCN and an acid. When the adipate was allowed to react with Et_4NCN (7 equivalents) in the presence of acetic acid (1 equivalent) at 50° C for 5 min. (equation 113), a mixture which contains dimethyl 1-cyanocyclobutane-1,2-dicarboxylate (*trans* and *cis*) and 2-cyano-2-methoxycarbonylcyclobutane-carboxylic acid (*trans* and *cis*) was obtained because six singlets for the protons of the methyl groups at δ 3.73, 3.75, 3.80, 3.83, 3.86 and 3.89 ppm in the NMR spectrum were observed. In another experiment, when the reaction was stirred at room temperature for 20 min., only dimethyl 1-cyanocyclobutane-1,2-dicarboxylate (*trans* and *cis* isomers) was obtained. Although the concentration of cyanide ion was increaseed, the reaction of dimethyl 2,5-dibromoadipate with cyanide ion in the buffer still formed the cyclization product.

In order to understand whether the cyclization can occur at lower temperature, we tried the reaction of dimethyl 2,5-dibromoadipate (0.4 N) with Et_4NCN (3.2 N) at -30° C in DMF, but the cyclization product was still produced. The reaction of dimethyl 2,5-dibromoadipate with Et_4NCN (10 equivalents) in the presence of acetic acid (5 equivalents) was also tried at -30° C. In this case, a mixture which contained the cyclization product and an



(114)

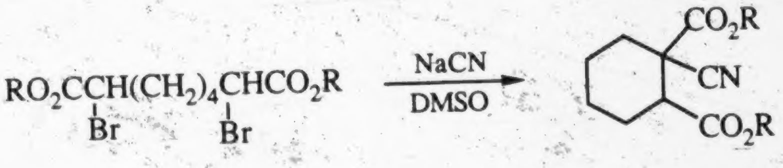
unknown compound was obtained (equation 114). The NMR spectrum of the unknown compound shows two singlets for the protons of the methyl esters at δ 3.76 and 3.77 ppm and two singlets for the protons of the acetyl groups at δ 2.14 and 2.15 ppm. The compound is probably dimethyl 2,5-diacetoxyadipate (*dl* and *meso* isomers). No attempt was made to isolate the compound.

The concentration of cyanide ion is increased by using Et_4NCN, but it is still low compared to the effective concentration of the internal nucleophile for the cyclization. As discussed earlier, the substitution of 2-bromoesters with cyanide ion can be controlled by using a buffer solution. On the other hand, the reaction of methyl α-bromophenylacetate with cyanide ion can be only controlled by higher concentrations of cyanide ion but by a buffer solution because of the higher acidity of the product, methyl α-cyanophenylacetate. For dimethyl 2,5-dibromoadipate, the cyclization takes place even at lower temperature. Once the mono-substituted α-cyanoester forms, it is deprotonated by cyanide ion and cyclizes immediately. The reaction of dimethyl 2,5-dibromoadipate with Et_4NCN (7 equivalents) is complete in 20 min. at room temperature, but the substitution of 2-

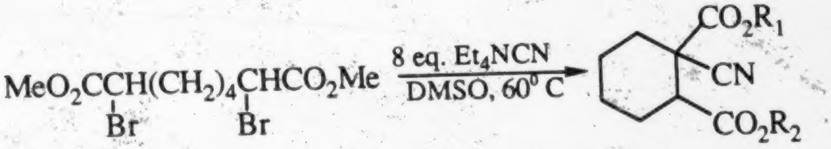
bromoesters with cyanide ion in the buffer system at room temperature takes about 5 hours. The cyclization is much faster than the substitution, which may explain why it is so difficult to prevent the cyclization.

4. Attempted synthesis of dimethyl 2,7-dicyanosuberate

The reaction of diethyl 2,7-dibromosuberates with sodium cyanide in ethanol was reported to form the cyclohexane (equation 115).[94,95] We also



(115)



(116)

1. $R_1 = CH_3$, $R_2 = H$.
2. $R_1 = H$, $R_2 = CH_3$.

tried the reaction of dimethyl 2,7-dibromosuberate with sodium cyanide in DMSO and obtained the cyclization product. However when the reaction of the suberate with 8 equivalents of tetraethylammonium cyanide was carried out at 60° C overnight, we isolated a carboxylic acid. The product was purified by recrystallization from benzene. The compound was identified as either 2-cyano-2-methoxycarbonylcyclohexane-carboxylic acid or 1-cyano-2-methoxycarbonylcyclohexane-carboxylic acid (equation 116). The acid is a white solid, which decomposes at 140° C. The NMR spectrum of the compound shows a singlet for the methyl protons at δ 3.76 ppm. The methine proton was observed as doublet of doublets (J = 4 Hz and 14 Hz). Two absorptions for the carbonyl groups in the IR spectrum appear at 1733 and 1713 cm^{-1}. The corresponding carbonyl groups appear at δ 173.88 and 172.03 ppm in the ^{13}C NMR spectrum. The pure compound was isolated in 48% yield. The hydrolysis only takes place at higher temperature.

VI. EXPERIMENTAL

All reactions were carried out at 21° C (room temperature) unless otherwise mentioned. All electron transfer reactions were performed under a positive atmosphere of argon. The solvents dimethylsulfoxide (DMSO), hexamethylphosphoramide (HMPA) and N,N-dimethylformamide (DMF) were used directly from commercially available products without further purification. HMPA should be handled with great care since it has been found to cause cancer in laboratory animals.[101] A rotary evaporator was used to remove solvents with a water aspirator. The remaining solvent could be removed with an oil pump.

Commercial silica (Merck 60F-254) thin layer chromatography (TLC) plates were used. TLC plates were visualized by uv light or with iodine. Flash chromatography[102,103] was performed by using silica gel (Merck type 9385).

Proton nuclear magnetic reasonance spectra (^{1}H NMR) were recorded with Bruker WP-80 (at 80 MHz) or Bruker WH-200 (at 200 MHz) spectrometers and chemical shifts are reported in parts per million (ppm) relative to internal tetramethylsilane (0.00 ppm). Carbon nuclear magnetic reasonance spectra (^{13}C NMR) were recorded with a Bruker WM-360 (at 90.56 MHz) spectrometer and are reported in ppm relative to tetramethylsilane (0.00 ppm). The following abbreviations are used in the text: δ, chemical shift; s, singlet; d, doublet; t, triplet; q, quartet; m, multiple; br, broad; J, coupling constant.

Elemental combustion analyses were performed in the microanalytical laboratories of the University of Alberta. Infrared spectra were recorded on a Nicolet 7000 FT-IR instrument. Mass spectra were recorded on a A.E.I MS 50 mass spectrometer at an ionizing potential 70 EV. A 15 w fluorescent lamp was used as the light source for photoinitiated electron transfer reactions.

The following usual workup procedure was employed for reactions discussed in this thesis. After a reaction was finished, the mixture was poured into 100 mL water and extracted with 3 × 30 mL of dichloromethane. The combined extracts were washed with water and dried ($MgSO_4$). The solvent was evaporated using a rotary evaporator. The remaning solvent could be removed with an oil pump. The residue was used for further purification.

1. Syntheses and Reactions of 2-Nitronitriles

2-*p*-Toluenesulfonyloxyacetonitrile

The procedure employed for the preparation of benzenesulfonyloxyacetonitrile[61] was followed using formaldehyde (37%, 9.7 mL, 0.13 mol), *p*-toluenesulfonyl chloride (25.0 g, 0.13 mol) in 30 mL of ether and sodium cyanide (5.90 g, 0.12 mol) in 30 mL of water. After workup, the residue was dissolved in dichloromethane-petroleum ether and cooled in dry ice to give a crude product (22.5 g, 89%), which was recrystallized from ethanol to afford a crystalline solid: mp 50-51° C (lit.[104] 51-52° C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.50 (s, 3 H), 4.78 (s, 2 H), 7.75 (d, J = 8 Hz, 2 H), 7.88 (d, J = 8 Hz, 2 H).

2-*p*-Toluenesulfonyloxypropanenitrile

A. The procedure employed for the preparation of 2-*p*-toluenesulfonyloxyacetonitrile was followed using *p*-toluenesulfonyl chloride (20.0 g, 0.105 mol), acetaldehyde (7.5 mL, 0.13 mol) in 30 mL of diethyl ether and sodium cyanide (5.90 g, 0.12 mol) in 30 mL of water. After workup, the residue was distilled to give a pale green oil (17.0 g, 72%): bp 135-136° C (0.5 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.69 (d, J = 6 Hz, 3 H), 2.50 (s, 3 H), 5.18 (q, J = 6 Hz, 1 H), 7.44 (d, J = 8 Hz, 2 H), 7.88

(d, J = 8 Hz, 2 H); MS exact mass *m/z* calcd for $C_{10}H_{11}NO_3S$: 225.0460; found 225.0461.

B. Lactonitrile (3.1 mL, 0.042 mol) was added in 40 mL of pyridine containing *p*-toluenesulfonyl chloride (16.0 g, 0.084 mol). The mixture was cooled to 0°C for 24 h., worked up by pouring into 200 mL of water, and extracted with 3 × 30 mL of dichloromethane. The combined extracts were rinsed with 1 N HCl, water and dried ($MgSO_4$). Removal of the solvent and distillation of the residue gave the product (6.5 g, 68%).

Attempted syntheses of 2-nitropropanenitrile

A. From 2-*p*-toluenesulfonyloxypropanenitrile: 2-*p*-Toluenesulfonyloxypropanenitrile (4.52 g, 0.020 mol) was added dropwise to a mixture of 30 mL of DMSO containing sodium nitrite (2.4 g, 0.035 mol) and anhydrous phloroglucinol (2.7 g, 0.021 mol). After being stirred for 24 h., the mixture was worked up in the usual way. Removal of the solvent by evaporation gave a residue, which contained mainly the starting material as observed from the NMR spectrum.

Without phloroglucinol, a large amount of bubbles was liberated during the reaction. No identifiable product could be isolated.

B. From 2-iodopropanenitrile: 2-Iodopropanenitrile was made by the reaction of 2-*p*-toluenesulfonyloxypropanenitrile (6.0 g, 0.027 mol) with potassium iodide (6.0 g) in 50 mL of acetone under reflux overnight. The flask should be kept in the dark to avoid decomposition of the iodo compound. The precipitate was removed by filtration and a deep brown solution was obtained after removal of acetone. The crude product was used directly without further purification; ^{1}H NMR (80 MHz, CDCl$_3$) δ 2.15 (d, J = 7 Hz, 3 H), 4.33 (q, J = 7 Hz, 1 H).

Silver nitrite[105] (3.10 g, 0.020 mol) was mixed with 30 mL of DMSO. The crude product 2-iodopropanenitrile obtained above was added to the mixture. After being stirred for 6 days in the dark, the precipitate was removed by filtration. The filtrate was poured into 100 mL of water and extracted with chloroform. Only the starting material 2-iodopropanenitrile (1.50 g, 31%) was recovered.

C. From 1-bromo-1-nitroethane: 1-Bromo-1-nitroethane[106] (4.62 g, 0.030 mol) was converted to the sodium salt using 40 mL of 1.5 N sodium hydroxide solution. A little sodium persulphate and sodium cyanide (4.90 g, 0.10 mol) were added into the resulting light yellow solution. A red solution was obtained in 15 min. and the solution became deep red brown in color half an hour later. The reaction was stirred 5 h. more and acidified by 1 N HCl. No identifiable product was isolated.

The reaction was also tried in DMSO, but a large amount of bubbles was liberated during the reaction. Again no identifiable product was obtained.

D. From 1-iodo-1-nitroethane: The procedure employed for the reaction of the bromo compound was followed using 1-iodo-1-nitroethane[106] (2.0 g, 0.010 mol), 20 mL of 1.5 N sodium hydroxide solution and sodium cyanide (2.0 g, 0.041 mol). Iodine was released during the reaction, but no identifiable product was isolated.

Attempted syntheses of nitroacetonitrile

p-Toluenesulfonyloxyacetonitrile (2.11 g, 0.010 mol) was added dropwise to the mixture of 15 mL of DMSO containing sodium nitrite (1.73 g, 0.025 mol) and anhydrous phloroglucinol (1.35 g, 0.011 mol). The reaction was stirred for 24 h. and worked up in the usual way. Only a little starting material was recovered. The reaction was also tried without phloroglucinol, no starting material was recovered.

Ethyl 2-bromo-2-nitropropanoate

Ethyl 2-nitropropanoate was made by the reaction of ethyl 2-bromopropanoate with sodium nitrite in the presence of phloroglucinol.[62]

Ethyl 2-nitropropanoate (16.0 g, 0.109 mol) was mixed with 40 mL of acetic acid containing sodium acetate (12.0 g, 0.15 mol). Bromine (5.8 mL, 0.113 mol) was added to the mixture dropwise with stirring. The reaction was worked up by pouring into 200 mL of water and extracted with benzene. The combined benzene extracts were washed with water and dried ($MgSO_4$). The residue, obtained after evaporation of the solvent, was distilled to give an oil (19.0 g, 80%): bp 56°C (0.3 mm) [lit.[107] bp 88°C (20 mm)]; ^1H NMR (80 MHz, $CDCl_3$) δ 1.33 (t, J = 6 Hz, 3 H), 2.40 (s, 3 H), 4.35 (q, J = 6 Hz, 2 H).

Ethyl 2,2-dinitropropanoate

Under argon, ethyl 2-bromo-2-nitropropanoate (2.0 g, 8.8 mml) was added dropwise to 15 mL of DMSO containing sodium nitrite (1.0 g, 14.5 mmol) and the mixture was stirred at 5° C for 3 h. The reaction was worked up in the usual way to give a liquid (1.10 g, 65%): bp 59-62° C (1 mm) [lit.[108] bp 45° C (0.1 mm)]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.38 (t, J = 6 Hz, 3 H), 2.43 (s, 3 H), 4.48 (q, J = 6 Hz, 2 H).

Ammonium salt of ethyl 2-nitropropanoate

Ethyl 2-nitropropanoate (0.50 g) was mixed with ammonium hydroxide (5 mL, 28-30%). The formed yellow solution was kept at -10° C for 5 h. White needles (0.50 g, 29%) were collected by filtration and identified by the NMR spectrum as the ammonium salt of the nitroester. ^{1}H NMR (80 MHz, D_2O) δ 2.28 (t, J = 6 Hz, 3 H) 2.08 (s, 3 H) 4.20 (q, J = 6 Hz, 2 H).

Ethyl 2-cyanopropanoate

A: Ethyl 2-bromopropanoate (5.0 g, 0.028 mol) was added dropwise to 150 mL of DMSO containing sodium cyanide (6.0 g, 0.122 mol). After being stirred for 5 h., the yellow mixture was worked up by pouring into 400 mL of water, acidifying with 1 N HCl, and extracting with chloroform. The combined chloroform extracts were rinsed with water and dried. The solvent was removed and distillation of the residue gave a liquid (1.38 g, 35%): bp

52°C (1.2 mm) [lit.[70] bp 77°C (9.5 mm)]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H), 1.58 (d, J = 7 Hz, 3 H), 3.58 (q, J = 7 Hz, 1 H), 4.28 (q, J = 7 Hz, 2 H).

After the distillation, some residue still remained in the flask. The residue could be distilled out at higher temperature 117° C (1.4 mm). It was identified as diethyl 2-cyanosuccinate. ^{1}H NMR (80 MHz, $CDCl_3$) 1.18-1.50 (m, 9 H), 1.62 (s, 3 H), 3.10 (q, J = 7 Hz, 1 H), 4.27 (q, J = 7 Hz, 4 H).

When the reaction was carried out in DMSO at 60-70° C, the 2-cyanoester was obtained in 40% yield and was isolated by distillation.

B: Ethyl 2-bromopropanoate (18.1 g, 0.10 mol) was added dropwise to a mixture of 200 mL of DMSO containing sodium cyanide (20.0 g, 0.41 mol) and acetic acid (17 mL, 0.28 mol). After being stirred for 5 h., the reaction was worked up by the above procedure to give the product (11.9 g, 94%).

Ethyl 2-cyano-2-methyl-3-iminopropanoate

A. The residue, obtained after ethyl 2-cyanopropanoate was distilled from the above reaction mixture B, was distilled at higher temperature (100° C, 1.2 mm). A little solid was obtained and recrystallized from hexane. No attempts were made to measure the yield. Sublimation under vacuum at 80° C gave a white solid: mp 113-114°C; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.28 (t, J = 6 Hz, 3 H), 2.00 (s, 3 H), 4.18 (q, J = 6 Hz, 2 H), 5.38-6.38 (b, 2 H); FT-IR ($CHCl_3$ cast) 3421, 2240, 1680, 1556, 1263, 1274 cm^{-1}; MS exact mass *m/z* calcd for $C_7H_{10}N_2O_2$: 154.0742; found 154.0745. Anal. Calcd for

$C_6H_{10}N_2O_2$: C, 54.34; H, 6.54; N, 18.17. Found: C, 54.30; H, 6.66; N, 18.07.

B. A mixture of ethyl 2-cyanopropanoate (0.64 g, 5 mmol), acetic acid (0.6 mL) and sodium cyanide (1.80 g) in 20 mL of DMSO was stirred at room temperature for 4 days. The mixture was poured into 50 mL of water and extracted with chloroform. After removal of the solvent by evaporation, the residue was distilled to give some starting material and the iminoester (45 mg, 6%), which was identified by the NMR spectrum.

Ethyl 2-cyano-2-nitropropanoate

A. Attempted synthesis from ethyl 2-bromo-2-nitropropanoate: Under argon, a mixture of sodium cyanide (0.49 g, 0.010 mol) and ethyl 2-bromo-2-nitropropanoate (2.0 g, 8.8 mmol) in 10 mL of DMSO was stirred overnight. The reaction was worked up in the usual way. After removal of the solvent, little residue was obtained, which contained ethyl 2-nitropropanoate, starting material and other products as determined from the NMR spectrum.

B. From ethyl 2-bromo-2-cyanopropanoate: The literature procedure[67] was modified by carrying out the reaction under argon at lower temperature. Under argon, ethyl 2-bromo-2-cyanopropanoate (23.0 g, 0.112 mol) was added dropwise to a mixture of 140 mL of DMF containing sodium nitrite (9.7 g, 0.14 mol) cooled to 0°C. The reaction was stirred at 0°C for 2 h. and worked up according to the literature procedure. Distillation gave the product (18.4 g, 96%): bp 48 -50°C (1 mm) [lit.[67] bp 99-101°C (13 mm)]; ^{1}H NMR

(80 MHz, $CDCl_3$) δ 1.38 (t, J = 7 Hz, 3 H), 2.19 (s, 3 H), 4.43 (q, J = 7 Hz, 2 H). IR (neat) 1770, 1580 cm^{-1}.

If the reaction was carried out at higher temperature (e.g. room temperature) for 3 h., a brown mixture was obtained (in this case, 60-79% product was still obtained). If the reaction was stirred at room temperature overnight, all the product decomposed. No attempts were made to identify the residue.

2-Nitropropanenitrile

A mixture of ethyl 2-cyano-2-nitropropanoate (9.31 g, 0.054 mol) in 40 mL of 3 N sodium hydroxide solution was stirred at 0-5° C until it became homogeneous. The solution was acidified carefully by acetic acid until there were no more bubbles liberated, followed by addition of 1 N HCl to adjust the pH to 1 at 0° C. The product was extracted with 3 × 50 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). Removal of the solvent gave the product (4.32 g, 80%) whose NMR spectrum was that of the pure compound: bp 28-29° C (0.1 mm); ^1H NMR (80 MHz, $CDCl_3$) δ 2.03 (d, J = 7 Hz, 3 H), 5.40 (q, J = 7 Hz, 1 H). Anal. Calcd for $C_3H_4N_2O_2$: C, 36.03; H, 4.03; N, 27.99. Found: C, 35.89; H, 3.97; N, 27.59.

The distillation temperature should be kept below 35° C because the compound is unstable. A light yellow liquid is obtained if it is left at room temperature for 1 h. The compound is best preserved in dry ice.

Attempted polymerizations of 2-nitropropanenitrile

A. 2-Nitropropanenitrile (0.20 g, 2 mmol) was converted into the sodium salt by treatment with 4 mL of 1 N sodium hydroxide solution. A small amount of sodium persulphate was added to the aqueous solution. No reaction was observed. 2-Nitropropanenitrile was recovered by acidifition.

Potassium ferricyanide and ferrous sulphate-hydrogen peroxide were also tried, but no apparent reaction was observed.

B. 2-Nitropropanenitrile (0.40 g, 4 mmol) was converted to the potassium salt by potassium carbonate (1.38 g, 10 mmol) in 10 mL of DMSO. A small amount of AIBN was added to the resulting light yellow solution at 60° C. After being stirred for 2 h., the reaction was worked up in the usual way, but no identifiable product was obtained.

Ethyl 2-bromo-2-cyanobutanoate

Ethyl 2-cyanobutanoate[72] was made in 90% yield by the condensation of ethyl cyanoacetate with acetaldehyde under catalytic hydrogenation: bp 54-55° C (0.1 mm) [lit.[109] bp 84-85° C (7 mm)]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 1.95 (d, J = 7 Hz, 2 H), 3.44 (t, J = 7 Hz, 1 H), 4.24 (t, J = 6 Hz, 2 H).

The bromination procedure employed for the preparation of ethyl 2-bromo-2-nitropropanoate was followed using ethyl 2-cyanobutanoate (68.9 g, 0.489 mol), 200 mL of acetic acid, sodium acetate (50.0 g) and bromine (26.3 mL, 0.513 mol). After workup, distillation of the residue gave a liquid (96.6

g, 84%): bp 54-55°C (0.2 mm) [lit.[110] bp 84.7°C (10 mm)]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.14 (t, J = 6 Hz, 3 H), 1.32 (t, J = 6 Hz, 3 H), 2.32 (q, J = 6 Hz, 2 H), 4.35 (q, J = 6 Hz, 2 H); IR (neat) 1752, 1235 cm^{-1}.

Ethyl 2-cyano-2-nitrobutanoate

The procedure employed for the preparation of ethyl 2-cyano-2-nitropropanoate was followed using ethyl 2-bromo-2-cyanobutanoate (97.0 g, 0.44 mol), 500 mL of DMF and sodium nitrite (36.4 g, 0.53 mol). The product (75.8 g, 93%) was obtained as a liquid: bp 53-54°C (0.1 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 1.38 (t, J = 6 Hz, 3 H), 2.59 (qd, J = 7 and 2 Hz, 2 H), 4.45 (q, J = 6 Hz, 2 H); IR (neat) 1770, 1580, 1230 cm^{-1}.

When the reaction was stirred at room temperature overnight, almost all the product decomposed. The reaction mixture became deep brown in color. Ethyl 2-hydroxyiminopropanoate was isolated in 20% yield.

Efforts to purify ethyl 2-cyano-2-nitrobutanoate by column chromatography on silica gel ($CHCl_3$ as an eluant) were unsuccessful. Some decomposition products were found on TLC after flash chromatography.

Ethyl 2-hydroxyiminopropanoate

Under argon, a mixture of ethyl 2-cyano-2-nitrobutanoate (2.0 g, 0.011 mol) and sodium nitrite (0.74 g) in 15 mL of DMF was stirred for 24 h. The mixture became red brown immediately, and was worked up by pouring into

50 mL of water and extracting with chloroform. Removal of the solvent left a residue, which was distilled (120° C, 0.5 mm) to give a white solid (0.30 g, 21%): mp 96-97°C (lit.[73] 97°C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.33 (t, J = 7 Hz, 3 H), 2.03 (s, 3 H), 4.25 (q, J = Hz, 2 H), 5.63-6.25 (br, 2 H). IR ($CHCl_3$ cast) 3238 (br), 1718, 1312, 1174, 1019 cm^{-1}.

When DMSO was used as a solvent, the decomposition proceeded faster. A large amount of bubbles was liberated during the reaction, but no identifiable product was obtained.

2-Nitrobutanenitrile

The procedure employed for the preparation of 2-nitropropanenitrile was followed by using ethyl 2-cyano-2-nitrobutanoate (18.6 g, 0.10 mol) and 80 mL of 4 N sodium hydroxide solution. Distillation gave a liquid (9.5 g, 83%): bp 25-27°C (0.5 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.09 (t, J = 7 Hz, 3 H), 2.26 (q, J = 7 Hz, 2 H), 5.24 (t, J = 7 Hz, 1 H); IR (neat) 2340, 1572 cm^{-1}.

2-Bromo-2-nitrobutanenitrile

Ethyl 2-cyano-2-nitrobutanoate (5.58 g, 0.030 mol) was hydrolyzed by treatment with 15 mL of 5 N sodium hydroxide solution. When a homogeneous solution was obtained, 20 mL of pentane was added. Bromine was added dropwise with stirring until color remained. The pentane layer was dried and evaporated. Distillation of the residue gave a liquid (5.32 g, 92%):

bp 30°C (0.4 mm) [lit.[60] bp 60-65°C (7 mm)]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.25 (t, J = 7 Hz, 3 H), 2.70 (q, J = 7 Hz, 2 H).

Methyl 2-bromo-2-cyanobutanoate

The procedure employed for the preparation of ethyl 2-cyanobutanoate was followed using methyl cyanoacetate (9.1 mL, 0.10 mol), acetaldehyde (10 mL 0.18 mol), 20 mL of acetic acid, 0.4 mL of piperidine and 0.5 g of 5% palladium on charcoal. After workup, the crude product, methyl 2-cyanobutanoate, was used directly for the next reaction. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.13 (t, J = 7 Hz, 3 H), 1.82-2.30 (m, 2 H), 3.50 (t, J = 7 Hz, 1 H), 3.83 (s, 3 H).

The crude methyl 2-cyanobutanoate was brominated with bromine (5.1 mL, 0.010 mol) using the procedure for the preparation of ethyl 2-bromo-2-cyanobutanoate. Distillation gave a liquid (14.3 g, 69%): bp 72-74°C (1 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.40 (q, J = 7 Hz, 2 H), 3.95 (s, 3 H).

Methyl 2-cyano-2-nitrobutanoate

The procedure employed for the preparation of the ethyl ester was followed using methyl 2-bromo-2-cyanobutanoate (27.4 g, 0.133 mol), sodium nitrite (14.0 g, 0.20 mol) and 150 mL of DMF. After workup, distillation gave the ester (16.6 g, 72%) as a liquid: bp 73-75°C (1 mm); ^{1}H

NMR (80 MHz, $CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 2.40 (qd, J = 7 and 2 Hz, 2 H), 3.98 (s, 3 H).

Methyl 2-bromo-2-cyanopentanoate

The procedure employed for the preparation of ethyl 2-cyanobutanoate was followed using methyl cyanoacetate (9.1 mL, 0.10 mol), propionaldehyde (8.70 g, 0.15 mol), 20 mL of acetic acid, 0.4 mL of piperidine and 0.5 g of 5% palladium on charcoal. The product, methyl 2-cyanopentanoate, was obtained as a colorless liquid (11.0 g, 78%): bp 66-68°C (1 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.40-1.75 (m, 2 H), 1.75-2.10 (m, 2 H), 3.55 (t, J = 7 Hz, 1 H), 3.83 (s, 3 H).

The bromination procedure for the preparation of ethyl 2-bromo-2-cyanobutanoate was followed by using methyl 2-cyanopentanoate (11.0 g, 0.078 mol), bromine (4.4 mL, 0.086 mol), 40 mL of acetic acid and sodium acetate (10.0 g). After workup, distillation gave a liquid (12.9 g, 75%): bp 78-80°C (1.2 mm); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.05 (t, J = 7 Hz, 3 H), 1.40-1.90 (m, 2 H), 2.33 (t, J = 7 Hz, 2 H), 3.95 (s, 3 H).

Methyl 2-cyano-2-nitropentanoate

The procedure employed for the preparation of ethyl 2-cyano-2-nitropropanoate was followed using methyl 2-bromo-2-cyanopentanoate (12.9 g, 0.059 mol), 80 mL of DMF and sodium nitrite (6.1 g, 0.088 mol). The product (10.0 g, 92%) was obtained as a liquid: bp 81-83°C (1 mm); ^{1}H

NMR (80 MHz, $CDCl_3$) δ 1.08 (t, J = 7 Hz, 3 H), 1.40-1.90 (m, 2 H), 2.40-2.70 (m, 2 H), 3.98 (s, 3 H).

Ethyl 2-cyano-2-nitropentanoate

The procedure employed for the preparation of the methyl ester was followed using ethyl cyanoacetate (16 mL, 0.15 mol), propionaldehyde (12.3 mL, 0.17 mol), 30 mL of acetic acid, 0.60 mL of piperidine and 0.5 g of 5% palladium on charcoal. The product, ethyl 2-cyanopentanoate, was obtained as a liquid (19.9 g, 82%): bp 54-56°C (0.3 mm); ^1H NMR (80 MHz, $CDCl_3$) δ 1.00 (t, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 1.40-1.75 (m, 2 H), 1.75-2.10 (m, 2 H), 3.50 (t, J = 7 Hz, 1 H), 4.24 (q, J = 7 Hz, 2 H).

The bromination of ethyl 2-cyanopentanoate (19.1 g, 0.123 mol) with bromine (7.0 mL, 0.137 mol) using the procedure for the preparation of the methyl ester gave ethyl 2-bromo-2-cyanopentanoate (26.5 g, 92%) as a liquid: bp 62-64°C (0.1 mm); ^1H NMR (80 MHz, $CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H), 1.38 (t, J = 7 Hz, 3 H), 1.30-1.80 (m, 2 H), 2.30 (t, J = 7 Hz, 2 H), 4.35 (q, J = 7 Hz, 2 H).

The reaction of ethyl 2-bromo-2-cyanopentanoate (25.8 g, 0.11 mol) with sodium nitrite (11.4 g, 0.165 mol) in 200 mL of DMF using the procedure for the preparation of the methyl ester gave a liquid (15.8 g, 72%): bp 58-60°C (0.1 mm); ^1H NMR (80 MHz, $CDCl_3$) δ 1.06 (t, J = 7 Hz, 3 H), 1.38 (t, J = 7 Hz, 3 H), 1.30-1.80 (m, 2 H), 2.35-2.37 (m, 2 H), 4.43 (q, J = 7 Hz, 2 H).

Reaction of methyl 2-cyano-2-nitrobutanoate with sodium nitrite (A) in DMF-d_7

The ester (20 mg) was dissolved in DMF-d_7 (0.5 mL) containing sodium nitrite (10 mg). The reaction was monitored by the NMR spectrum. Some bubbles formed in 10 min. After 30 min. a broad peak at δ 8.50-8.75 ppm appeared and changed position with time. The splitting for the ethyl group became complex. There were several peaks between δ 3.50-4.00 ppm for the methyl protons of the ester group and the intensity of the peak at δ 3.63 ppm increased with time. After 20 h., all the peaks between δ 3.50-4.00 ppm disappeared except the peak at δ 3.63 ppm.

(B). In DMSO-d_6. The ester (43 mg) and sodium nitrite (27 mg) were mixed in 0.7 mL of DMSO-d_6. A large amount of bubbles was observed during the reaction. The starting material completely disapperaed after 160 min. as observed from the NMR spectrum. Also only the peak at δ 3.63 ppm for the methyl protons of the ester group remained after 3 h. The splitting of the ethyl group also became complex.

Attempted polymerization of 2-nitrobutanenitrile

A. 2-Nitrobutanenitrile (1.74 g, 0.013 mol) was dissolved in 10 mL of aqueous solution containing potassium carbonate (1.8 g, 0.013 mol). A small amount of sodium persulphate was added to the resulting light yellow solution (3 mL). The reaction was stirred overnight. The starting material was recovered by acidification.

Potassium ferricyanide and ferrous sulphate-hydrogen peroxide were also used for the above reaction, but still no reaction was observed.

B. A small amount of AIBN was added to 15 mL of DMF containing 2-nitrobutanenitrile (1.47 g) and potassium carbonate (1.30 g). The mixture was stirred at 60° C for 2 h. and became deep brown gradually. The reaction was worked up in the usual way, but no identifiable product was obtained.

C. 2-Nitrobutanenitrile (1.14 g) was converted to the potassium salt by treatment with potassium carbonate (0.70 g) in 10 mL of DMSO. A small amount of 2-bromo-2-nitrobutanenitrile was added to the resulting light yellow mixture. No reaction was observed.

In another attempt, 2-bromo-2-nitrobutanenitrile (1.93 g, 10 mmol) was added. After being stirred overnight, the red reaction mixture was worked up by pouring into 50 mL of water, acidifying with 1 N HCl, and extracting with chloroform. 2-Nitrobutanenitrile was recovered.

2,3-Dicyano-2,3-dinitrobutane

2-Nitropropanenitrile (0.72 g, 7.2 mmol) was converted to the potassium salt by treatment with potassium bicarbonate (1.0 g, 12 mmol) in 20 mL of water. Potassium ferricyanide (5.0 g) and sodium persulphate (2.0 g) were added to the aqueous solution. The reaction mixture was stirred for 48 h. The precipitate was collected and recrystallized from hexane-THF to give the product (0.30 g, 42%). Sublimation under vacuum (0.5 mm) at 100° C gave a white solid: mp 144°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.36 (s), 2.39 (s). Anal. Calcd for $C_6H_6N_4O_4$: C, 36.37; H, 3.05; N, 28.28. Found: C, 36.38; H, 3.08; N, 28.12.

3,4-Dicyano-3,4-dinitrohexane

2-Nitrobutanenitrile (1.0 g, 8.8 mmol) was converted to the anion with potassium carbonate (1.21 g) in 50 mL of water. Potassium ferricyanide (7.25 g) and sodium persulphate (2.1 g) were added to the aqueous solution. After stirring for 3 days, collection by filtration gave the crude product (0.50 g, 45%) as a mixture of *dl* and *meso* isomers. The mixture was recrystallized from ethanol. The crystals were collected and further purified by sublimation under vacuum (0.5 mm) at 100° C to give a white solid: mp 142°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26 (t, J = 7 Hz, 6 H), 2.25 (qd, J = 7 and 14 Hz, 2 H), 2.82 (qd, J = 7 and 14 Hz, 2 H). Anal. Calcd for $C_8H_{10}N_4O_4$: C, 42.48; H, 4.46; N, 24.77. Found: C, 42.26; H, 4.51; N, 24.78.

The filtrate was concentrated and the residue was recrystallized from ethanol again. The crystals contained mainly another isomer (over 90%) as estimated from the integration of the NMR spectrum. Sublimation under vacuum at 100° C gave the mixture as a white solid: mp 118-120°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.34 (t, J = 7 Hz, 6 H), 2.33 (m, J = 7 Hz, 2 H), 2.72 (m, J = 7 Hz, 2 H). Anal. Calcd for $C_8H_{10}N_4O_4$: C, 42.48; H, 4.46; N, 24.77. Found: C, 42.41; H, 4.54; N, 24.90.

4,5-dicyano-4,5-dinitrooctane

Ethyl 2-cyano-2-nitropentanoate (4.50 g, 0.024) was hydrolyzed by treatment with sodium hydroxide (5.20 g) in 50 mL of water. When the homogeneous solution was obtained, the aqueous solution was acidified with acetic acid and then 1 N HCl at 0°C. The product 2-nitropentanenitrile was extracted with 3 × 40 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). After removal of the solvent, the crude product, 2-nitropentanenitrile, was converted to the potassium salt with potassium carbonate (3.0 g) in 40 mL of water. Potassium ferricyanide (7.25 g) and sodium persulphate (5.20 g) were added to the aqueous solution. The reaction mixture was stirred for 2 days. The crude product (0.70 g, 28%) was obtained by filtration and purified by recrystallization from hexane. Sublimation under vacuum (0.5 mm) at 100° C gave a white solid: mp 86-88°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, J = 7 Hz, 3 H), 1.09 (t, J = 7 Hz, 3 H), 1.24-1.60 (m, 2 H), 1.68-2.00 (m, 2 H), 2.02-2.30 (m, 2 H), 2.54-2.80 (m, 2 H). Anal. Calcd for $C_{10}H_{14}N_4O_4$: C, 47.24; H, 5.55; N, 22.04. Found: C, 47.09; H, 5.53; N, 22.06.

Reaction of the lithium salt of 2-nitropropane (a) with 2,3-dicyano-2,3-dinitrobutane

Under argon, a solution of 2,3-dicyano-2,3-dinitrobutane (50 mg, 0.25 mmol) and the lithium salt of 2-nitropropane (0.20 g, 2.1 mmol) in 5 mL of HMPA was stirred overnight. The reaction was worked up by pouring into

20 mL of water, and extracting with 3 × 20 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). Evaporation of the solvent gave a residue. A measured amount of *p*-dimethoxybenzene was mixed with the residue. The mixture was dissolved in 0.6 mL of $CDCl_3$. The yield of the product 2,3-dimethyl-2,3-dinitrobutane (32 mg, 73%) was estimated from the integration of the NMR spectrum. Only the signals of 2,3-dimethyl-2,3-dinitrobutane and *p*-dimethoxybenzene were observed in the NMR spectrum.

(b) with 3,4-dicyano-3,4-dinitrohexane. In HMPA (5 mL) 50 mg (0.22 mmol) of the dimer reacted with the lithium salt of 2-nitropropane (0.10 g, 1 mmol) overnight when the procedure of preceeding experiment was followed. Workup in the usual way gave 34 mg (87% yield) of 2,3-dimethyl-2,3-dinitrobutane, which was estimated by using the above method.

2. Syntheses and Reactions of Model Compounds for the Polymerization

2-Nitro-1-phenyl-1-propene

The procedure employed for the synthesis of 1-*O*-methoxyphenyl-2-nitropropene was followed.[77] A solution of benzaldehyde (21.2 g, 0.20 mol) in 100 mL of toluene, nitroethane (41.0 g) and 0.5 mL of *n*-butylamine was refluxed for 24 h. and 3.6 mL of water was removed via a Dean-Stark apparatus. The solvent was evaporated and the residue was recystallized from methanol to give yellow needles (27.6 g, 85%): mp 63-64°C (lit.[76a] 64-65° C); ^{1}H NMR (80 MHz, CDCl$_3$) δ 2.45 (s, 3 H), 7.43 (s, 5 H), 8.08 (s, 1 H).

2-Nitro-1-phenylpropane

The compound was made in 91% yield by the reaction of 2-nitro-1-phenylpropene with sodium borohydride in THF.[78] Distillation gave a liquid: bp 74-76°C (0.5 mm) [lit.[111] 81.5-82°C (0.8 mm)]; ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.54 (d, J = 7 Hz, 3 H), 3.00 (dd, J = 7, 14 Hz, 1 H), 3.30 (dd, J = 7, 14 Hz, 1 H), 4.77 (m, J = 7 Hz, 1 H), 7.12-7.18 (m, 2 H), 7.24-7.38 (m, 3 H).

2,2-Dinitro-1-phenylpropane

The lithium salt of 2-nitro-1-phenylpropane was made in 98% yield using the procedure for the preparation of the lithium salt of 2-nitropropane[112] except that lithium methoxide was used, which was generated by the reaction of lithium with methanol.

The following procedure is based on a general method for the synthesis of gem-dinitro compounds.[15] Sodium nitrite (15.0 g, 0.22 mol), potassium ferricyanide (3.1 g) and sodium persulphate (11.3 g) were added to a mixture of the lithium salt of 2-nitro-1-phenylpropane (8.0 g, 0.047 mol) in 200 mL of water and 100 mL of dichloromethane. After being stirred overnight, the dichloromethane layer was separated, rinsed with water and dried ($MgSO_4$). Removal of the solvent and recrystallization of the residue from hexane gave white needles (6.8 g, 69%): mp 72-73°C; FT-IR ($CHCl_3$ cast) 1559 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.02 (s, 3 H,) 3.84 (s, 2 H), 7.12-7.32 (m, 2 H), 7.34-7.40 (m, 3 H). Anal. Calcd for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.80; N, 13.33. Found: C, 51.34; H, 4.79; N, 13.25.

2,3-Dimethyl-2,3-dinitro-1-phenylbutane

A. Under argon, a solution of 2,2-dinitro-1-phenylpropane (210 mg, 1 mmol) and the lithium salt of 2-nitropropane (0.19 g, 4 mmol) in 10 mL of DMSO was stirred overnight. The reaction was worked up by pouring into 100 mL of water. The precipitate (0.22 g, 87%) was collected. Recrystallization from hexane gave a white crystalline solid: mp 119-120°C;

^{1}H NMR (200 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 1.74 (s, 3 H), 1.95 (s, 3 H), 3.28 (d, J = 7 Hz, 1 H), 3.90 (d, J = 7 Hz, 1 H), 7.00-7.10 (m, 2 H), 7.25-7.35 (m, 3 H). Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.11. Found: C, 57.37; H, 6.44 ; N, 11.01.

The reaction was monitored by TLC (1% methanol in chloroform as an eluant). It is complete in 45 min. as observed from TLC by the disappearance of 2,2-dinitro-1-phenylpropane.

B. From the tetraethylammonium salt: Under argon, 2-nitropropane (0.27 g, 3 mmol) was converted to the tetraethylammonium salt in 10 mL of DMSO with 20% Et_4NOH solution (2.20 g, 3 mmol). 2,2-Dinitro-1-phenylpropane (210 mg, 1 mmol) was added to the resulting light yellow solution. The reaction was illuminated with a 15 w fluorescent lamp for 20 min. The product (0.22 g, 87%) was isolated by precipitation with water.

2-Iodo-2-nitro-1-phenylpropane

2-Nitro-1-phenylpropane (1.52 g, 9.2 mmol) was converted to the tetraethylammonium salt with 20% Et_4NOH (6.84 g, 9.3 mmol) in 20 mL of methanol. The solution was added dropwise to 30 mL of methanol containing iodine (2.34 g, 0.010 mol). When the addition was complete, the solution was cooled to 0° C for 1 h. in the dark. The precipitate was collected and recrystallization from methanol gave yellow crystals: mp 84-85° C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.34 (s, 3 H), 3.66 (d, J = 14 Hz, 1 H), 4.00 (d, J = 14 Hz, 1 H), 7.08-7.18 (m, 2 H), 7.22-7.32 (m, 3 H). MS exact mass *m/z* calcd for $C_9H_{10}INO_2$: 290.9716; found 290.9752.

2,3-Dimethyl-2,3-dinitro-1,4-diphenylbutane

A. Under argon, a solution of 2,2-dinitro-1-phenylpropane (210 mg, 1 mmol) and the lithium salt of 2-nitro-1-phenylpropane (340 mg, 2 mmol) in 10 mL of HMPA was stirred overnight. The reaction was worked up by pouring into 100 mL of water. The precipitate was collected. The dimer (0.30 g, 91%) was obtained as a mixture of *dl* and *meso* isomers.

The mixture was separated by extraction with benzene. The insoluble material was removed by filtration. Evaporation of the solvent gave a residue, which was purified by recrystallization from hexane as white needles: mp 188-190°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.38 (s, 6 H), 2.70 (d, J = 7 Hz, 2 H), 4.08 (d, J = 7 Hz, 2 H), 7.02-7.08 (m, 4 H), 7.28-7.36 (m, 6 H). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.62; H, 6.13; N, 8.50.

The benzene insoluble material was collected. It is only slightly soluble in chloroform. Recrystallization from THF gave a white crystalline solid: mp 230-232°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.58 (s, 6 H), 3.08 (d, J = 7 Hz, 2 H), 4.04 (d, J = 7 Hz, 2 H), 7.04-7.12 (m, 4 H), 7.28-7.36 (m, 6 H). Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.79; H, 6.10; N, 8.47.

The reaction was monitored by TLC (eluant benzene:hexane:methanol = 20:78:2). At 21°C, the reaction is complete in 5 h.; at 50°C, 2.5 h., but only 15 min. is required under illumination.

B. By iodine coupling with the ammonium salt: General procedure: Under argon, 2-nitro-1-phenylpropane was converted to the tetraethylammonium salt by equal equivalents of Et_4NOH solution in 15 mL of solvent. Iodine (1 mmol) was added to the solution and the reaction was illuminated for 20 min. The product was isolated by precipitation with water and collected by filtration. The dimer was dried and the yield measured according to weight. The yield of the dimer obtained in various solvents with different ratios of iodine and 2-nitro-1-phenylpropane is summarized in Table I.

Table I. The yield of the dimer obtained in various solvents with different ratios of iodine and 2-nitro-1-phenylpropane.

2-Nitro-1-phenylpropane (mmol)	I_2 (mmol)	Solvent	Yield (%)
3	1	HMPA	91
2	1	HMPA	85
3	1	DMSO	91
3	1	CH_3CN	91
2	1	CH_3CN	88
3	1	THF	91
2	1	THF	82

C. By the reaction of 2-iodo-2-nitro-1-phenylpropane with the ammonium salt. General procedure: Under argon, the ammonium salt of 2-nitro-1-phenylpropane was generated using the above method. 2-Iodo-2-nitro-1-phenylpropane (1 mmol) was added to the solution. The reaction was illuminated for 20 min. The product was isolated by precipitation with water and dried by air. The yield was measured by weight. The yield of the dimer obtained with different solvents and reaction times is summarized in Table II.

Table II. The yield of the dimer obtained with different solvents and reaction times.

2-Iodo-2-nitro-1-phenylpropane (mmol)	The ammoniun salt (mmol)	Time (min.)		Solvent (%)
1	1	20	HMPA	75
1	1	20	DMSO	75
1	1	10	CH_3CN	91
1	1	5	CH_3CN	91

D. By the reaction of 2,2-dinitro-1-phenylpropane with the lithium salt or the ammonium salt. General procedure: Under argon, the ammonium salt was generated by using the above method. A mixture of 2,2-dinitro-1-phenylpropane (0.21 g, 1 mmol) and the lithium salt or the ammonium salt of 2-nitro-1-phenylpropane in 15 mL of solvent was illuminated with stirring for 20 min. The product was isolated isolated using the above method and the yield measured by weight. The yield of the dimer obtained in different solvents for the reaction of the lithium salt or the ammonium salt with the gem-dinitro compound is summarized in Table III.

Table III. The yield of the dimer obtained in different solvents for the reaction of the lithium salt or the ammonium salt with the gem-dinitro compound.

The lithium salt (mmol)	The ammonium salt (mmol)	Solvent	Yield (%)
2		HMPA	91
2		DMSO	91
1		HMPA	75[a]
	2	CH_3CN	0[b]
	2	THF	0[b]

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a. Longer illumination (overnight) gave only 79% yield.

b. Only 16% conversion was observed after illumination for 5 h. as determined from the NMR spectrum. Small amount iodine was added, but only 30% conversion after 8 h.

Determination of disproportionation yield

A. From the lithium salt: Under argon, a mixture of 2,2-dinitro-1-phenylpropane (210 mg, 1 mmol) and the lithium salt of 2-nitro-1-phenylpropane (0.34 g, 2 mmol) in 10 mL of HMPA was illuminated with stirring for 20 min. Water (50 mL) was added, and the precipitate was removed by filtration. The filtrate was extracted with 3 × 20 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). Removal of the solvent by evaporation left a residue, which was examined by the NMR spectrum. *p*-Dimethoxybenzene was used as an internal standard. The yield of the disproportionation product, 2-nitro-1-phenylpropane (8.4 mg, 5.1%), was estimated by measuring the ratio of the area of the methine proton of the product to the methyl protons of *p*-dimethoxybenzene from the NMR spectrum.

In the blank test, the lithium salt of 2-nitro-1-phenylpropane (0.34 g, 2 mmol) was dissolved in 20 mL of water, and extracted with dichloromethane (3 × 20 mL). The solvent was evaporated. A measured amount of *p*-dimethoxybenzene was added into the residue. 2-Nitro-1-phenylpropane was not detected from the NMR spectrum.

B. From the tetraethylammonium salt (in 1:1 ratio) Under argon, 2-nitro-1-phenylpropane (0.330 g, 2 mmol) was converted to the tetraethylammonium salt by 18.4% Et_4NOH (1.76 g, 2.2 mmol) in 10 mL of HMPA. Iodine (279 mg, 1.1 mmol) was added to the resulting light yellow solution. After being stirred for 20 min. with illumination, the reaction was worked up according to the above procedure. The yield of disproportionation product was estimated to be 2.4%.

C. From the tetraethylammonium salt (in 1:1.5 ratio). The above procedure B was followed using 2-nitro-1-phenylpropane (0.50 g, 0.003 mol), 18.4% Et_4NOH (2.48 g, 0.0031 mol) in 15 mL of HMPA and iodine (254 mg, 0.001 mol). The yield of the disproportionation product was estimated to be 0.5%.

In the blank test, 2-nitro-1-phenylpropane (0.50 g, 0.003 mol), 18% Et_4NOH (2.80 g, 0.0034 mol) and 15 mL of HMPA were used. After workup, no 2-nitro-1-phenylpropane was recovered as determined from the NMR spectrum.

The potassium salt of 2-nitro-1-phenylpropane

2-Nitro-1-phenylpropane (0.83 g, 5 mmol) was dissolved in 20 mL of methanol containing potassium *t*-butoxide (0.56 g, 5 mmol). The potassium salt (1.0 g, 100%) was isolated using the same procedure for the lithium salt. ^1H NMR (80 MHz, D_2O) δ 1.74 (s, 3 H), 3.62 (s, 2 H), 7.10-7.30 (m, 5 H).

The tetraethylammonium salt of 2-nitro-1-phenylpropane

A. A solution of 2-nitro-1-phenylpropane (0.83 g, 5 mmol) and 20% tetraethylammonium hydroxide solution (3.68 g, 5 mmol) in 20 mL of methanol was stirred for a while. After the solvent was removed by evaporation, a light yellow syrup was obtained; ^{1}H NMR (200 MHz, D_2O) δ 1.13 (t, J = 7 Hz, 12 H), 1.75 (s, 3 H), 3.08 (q, J = 7 Hz, 8 H), 3.78 (s, 2 H), 7.10-7.40 (b, 5 H).

B. The potassium salt of 2-nitro-1-phenylpropane (0.51 g, 2.5 mmol) was dissolved in 10 mL of 1-propanol. A little methanol was added until the potassium salt was dissolved. Anhydrous tetraethylammonium chloride (0.50 g, 3 mmol) was added to the solution and the solution stirred for a while. The precipitate was removed and the solvent evaporated. The crude product (0.56 g, 76%) was obtained as a yellow solid. A little tetraethylammonium chloride and 1-propanol were detected from the NMR spectrum.

2,3-Dimethyl-1,4-diphenyl-2-butene

A. The following procedure is based on a general method for the elimination of vicinal dinitro groups to an alkene.[36] A mixture of *dl* and *meso* 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane (0.50 g, 0.15 mmol) and sodium sulfide ($Na_2S{\cdot}10H_2O$, 1.5 g) in 15 mL of DMF was stirred under illumination for 24 h. The mixture was worked up by pouring into 50 mL of water and extracting with dichloromethane. After the solvent was evaporated, the crude product (0.30 g, 83%) was obtained as a mixture of *trans* and *cis* isomers in a 1:1 ratio. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.64 (s, 3 H), 1.72 (s, 3 H), 3.46 (s, 2 H), 3.52 (s, 2 H), 7.12-7.36 (m, 10 H).

The mixture was distilled and one of the isomers crystallized in the distillate, bp 134-138°C (0.5 mm). The crystals were collected by filtration and rinsed with 10 mL of pentane. Recrystallization from pentane afforded a white crystalline solid: mp 48-50° C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.72 (s, 6 H), 3.46 (s, 4 H), 7.14-7.36 (m, 10 H). Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.70; H, 8.23. MS exact mass *m/z* calcd for $C_{18}H_{20}$: 236.1565; found 236.1562.

The solvent in the filtrate was evaporated. The residue has a strong hydrogen sulfide smell. The mixture is still a mixture (9:1 ratio) as observed from the NMR spectrum. No attempt was made to purify the isomer. ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 6 H), 3.52 (s, 4 H), 7.12-7.36 (m, 10 H). MS exact mass *m/z* cacld for $C_{10}H_{20}$: 236.1565; found 236.1564.

When the pure *dl* isomer of the dimer was used for the reaction, the product was still a mixture of *trans* and *cis* isomers in about 1:1 ratio as observed from the NMR spectrum.

B. A mixture of 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane (160 mg, 0.5 mmol) and the lithium salt of 2-nitro-1-phenylpropane (0.26 g, 1.5 mmol) in 5 mL of HMPA was illuminated for 5 h. The reaction was worked up by pouring into 50 mL of water. After the precipitate was removed, the filtrate was extracted with chloroform. Evaporation of the solvent gave a residue, which was examined by the NMR spectrum. It contained *trans* and *cis* alkene in about 1:1 ratio and a little starting material.

C. A mixture of 2,2-dinitro-1-phenylpropane (1 mmol, 0.21 g) and the lithium salt of 2-nitro-1-phenylpropane (3 mmol, 0.51 g) in 10 mL of HMPA was stirred under illumination for 5 h. The reaction was worked up according to the above method. The signals of the *trans* and *cis* alkene in about 1:1 ratio and little dimer were observed from the NMR spectrum. No yield was taken for the reaction.

D. A solution of 2,3-dimethyl-2,3-dinitro-1,4-diphenylbutane (0.16 g, 0.5 mmol) and the lithium salt of 2-nitropropane (0.20 g, 2.1 mmol) in 5 mL of HMPA was illuminated with stirring for 5 h. The reaction was worked up in the usual way. The residue, obtained after removal of the solvent, was recrystallized from ethanol to give 2,3-dimethyl-2,3-dinitrobutane (50 mg, 57%). The residue left behind after the recrystallization was examined by the NMR spectrum. It still contained 2,3-dimethyl-2,3-dinitrobutane and a little alkene. No signals for the cross coupling product 2,3-dimethyl-2,3-dinitro-1-phenylbutane were observed from the NMR spectrum.

1,4-Bis(2-nitro-1-propenyl)benzene

The compound was made by refluxing a solution of terephthaldicarboxyaldehyde (21.44 g, 0.16 mol), nitroethane (64.0 g) and 0.4 mL of amylamine for 24 h.[85] The product was precipitated by addition of 95% ethanol and purified by recystallization from 95% ethanol to give yellow crystals (29.5 g, 74%): mp 119-120°C [lit.[85] 120° C]; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.50 (s, 6 H), 7.52 (s, 4 H), 8.08 (s, 2 H).

1,4-Bis(2-nitropropyl)benzene

The following procedure is based on a general method for the reduction of α-nitroalkenes.[78] Sodium borohydride (7.13 g) was added portionwise to the solution of 675 mL of THF and 75 mL of methanol containing 1,4-bis(2-nitropropyl)benzene (18.6 g, 0.075 mol). The mixture was stirred for 3 h.

After 200 mL of water was added, the mixture was stirred for 3 h. more and then acidified slowly by acetic acid. The solvent was evaporated and the product collected by filtration. Recrystallization from methanol gave a white crystalline solid (16.6 g, 88%): mp 112-113°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.54 (d, J = 7 Hz, 6 H), 2.98 (dd, J = 7, 14 Hz, 2 H), 3.30 (dd, J = 7, 14 Hz, 2 H), 4.76 (m, J = 7 Hz, 2 H), 7.10 (s, 4 H). Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.11; H, 6.39; N, 11.11. Found: C, 57.39; H, 6.54; N, 11.24.

The dilithium salt of 1,4-bis(2-nitropropyl)benzene

The following procedure is based on a general method for the synthesis of lithium nitronates.[112] Lithium (0.694 g, 0.10mol) was dissolved in 50 mL of methanol. 1,4-Bis(2-nitropropyl)benzene (12.6 g, 0.050 mol) was added to the solution and the mixture stirred until it dissolved. The solvent was evaporated until precipitate just appeared. A little methanol was added to redissolve the precipitate. A little acetonitrile (20 mL) was added slowly followed by addition of 400 mL of diethyl ether. The dilithium salt (12.6 g, 95%) was collected, dried under vacuum, and was obtained as a white powder: ^{1}H NMR (80 MHz, D_2O) δ 1.75 (s, 6 H), 3.65 (s, 4 H), 7.12 (s, 4 H).

The dipotassium salt of 1,4-bis(2-nitropropyl)benzene

1,4-Bis(2-nitropropyl)benzene (1.26 g, 5 mmol) was dissolved in 30 mL of methanol. Potassium *t*-butoxide (1.20 g, 10.7 mmol) was added to the solution. The solvent was evaporated until the precipitate just appeared. The dipotassium salt (1.65 g, 100%) was isolated according to the above method as a light yellow solid: ^{1}H NMR (80 MHz, D_2O) δ 1.72 (s, 6 H), 3.60 (s, 4 H), 7.06 (s, 4 H).

1,4-Bis(2,2-dinitropropyl)benzene

The following procedure is based on a general method for the synthesis of gem-dinitro compounds.[14,15] The dilithium salt of 1,4-bis(2-nitropropyl)-benzene (0.66 g, 2.5 mmol) was dissolved in 40 mL of water. Sodium nitrite (1.40 g, 0.20 mol), potassium ferricyanide (0.33 g) and sodium persulphate (1.2 g) were added to the solution. The mixture was stirred for 5 h. The crude product (0.63 g, 73%) was collected by filtration. Recrystallization from benzene gave a white crystalline solid: mp 175-176°C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 2.04 (s, 6 H), 3.91 (s, 4 H), 7.09 (s, 4 H). Anal. Calcd for $C_{12}H_{14}N_4O_8$: C, 42.10; H, 4.12; N, 16.40. Found: C, 42.07; H, 4.13; N, 16.35.

1,4-Bis(2-bromo-2-nitropropyl)benzene

The dilithium salt of 1,4-bis(2-nitropropyl)benzene (0.66 g, 2.5 mmol) was dissolved in 30 mL of water and bromine (0.88 g, 5.5 mmol) was added dropwise to the solution. The reaction mixture was stirred for half an hour. The crude product (0.98 g, 95%) was collected by filtration. Recrystallization from ethanol gave needles: mp 187°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.16 (s, 6 H), 3.52 (d, J = 14 Hz, 2 H), 3.83 (d, J = 14 Hz, 2 H), 7.14 (s, 4 H). Anal. Calcd for $C_{12}H_{14}Br_2N_2O_4$: C, 35.13; H, 3.44; N, 6.83; Br, 38.97. Found: C, 35.12; H, 3.45; N, 6.93; Br, 39.13.

1,4-Bis(2,3-dimethyl-2,3-dinitrobutyl)benzene

A. Attempted synthesis from 1,4-bis(2-bromo-2-nitropropyl)benzene: Under argon, a solution of 1,4-bis(2-bromo-2-nitropropyl)benzene (0.41 g, 1 mmol) and the lithium salt of 2-nitropropane (0.40 g, 4.2 mmol) in 20 mL of DMSO was stirred overnight. The mixture was poured into 100 mL of water and then acidified with 1 N HCl. The precipitate was collected and examined by NMR (DMSO-d_6). It contained 2,3-dimethyl-2,3-dinitrobutane, 1,4-bis(2-nitropropyl)benzene and other products.

B. From 1,4-bis(2,2-dinitropropyl)benzene: Under argon, a solution of 1,4-bis(2,2-dinitropropyl)benzene (342 mg, 1 mmol) and the lithium salt of 2-nitropropane (0.40 g, 4.2 mmol) in 10 mL of HMPA was stirred for 24 h. The red brown solution was poured into 100 mL of water and the precipitate was collected to give the crude product (0.32 g, 75%). The crude product is insoluble in chloroform or DMSO. Recrystallization from nitroethane gave a white solid, mp 240°C (dec.). Anal. Calcd for $C_{18}H_{26}N_4O_8$: C, 50.70; H, 6.15; N, 13.13. Found: C, 50.42; H, 6.06; N, 13.04.

1,4-Bis(2,3-dimethyl-4-phenyl-2-butenyl)benzene

Under argon, a solution of 1,4-bis(2,2-dinitropropyl)benzene (342 mg, 1 mmol) and the lithium salt of 2-nitro-1-phenylpropane (0.51 g, 3 mmol) in 15 mL of HMPA were stirred for 48 h. The product (0.48 g, 83%) was isolated by precipitation with water. The product was believed to be 1,4-bis(2,3-dimethyl-2,3-dinitro-4-phenylbutyl)benzene and was recrystallized from nitroethane-DMSO at 110°C five times. The analysis for the ratio of carbon was still low; mp 210° C (dec.). Anal. Calcd for $C_{30}H_{34}N_4O_8$: C. 62.27; H, 5.92; N, 9.69. Found: C, 61.84; H, 5.96; N, 9.53.

The above reaction was repeated. After stirring for 48 h., sodium sulfide ($Na_2S{\cdot}10H_2O$, 1.05 g) was added directly to the solution. The reaction mixture was stirred under illumination for 24 h., and worked up by pouring into 100 mL of water. One of the products was collected by filtration. The crude product was obtained (0.11 g, 28%) whose NMR spectrum was that of the pure compound. Recrystallization from hexane gave white crystals: mp 130-132°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.74 (s, 12 H), 3.45 (s, 4 H), 3.48 (s, 4 H), 7.10 (s, 4 H), 7.14-7.36 (m, 10 H). Anal. Calcd for $C_{30}H_{34}$: C, 91.31; H, 8.69. Found: C, 91.33; H, 8.48. MS exact mass *m/z* calcd for $C_{30}H_{34}$: 394.2662; found 394.2660.

The filtrate was extracted with 3 × 30 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). After removal of the solvent, the residue changed color gradually. Attempts to purify the residue by recrystallization were unsuccessful. ^1H NMR ($CDCl_3$) δ 1.66(s), 1.74 (s), 1.80 (s), 3.44 (s), 3.46 (s), 3.50 (s), 3.54 (s), 3.68 (s) 3.72 (s).

The tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene

A. 1,4-Bis(2-nitropropyl)benzene (1.26 g, 0.5 mmol) was dissolved in 40 mL of methanol. Tetraethylammonium hydroxide (7.40 g, 20%) was added to the solution and the resulting light yellow solution was stirred for a while. The residue, obtained after evaporation of the solvent, was a light yellow syrup: ^1H NMR (200 MHz, D_2O) δ 1.10-1.20 (three triplets, 24 H), 2.74 (s, 6 H), 3.12 (q, J = 7 Hz, 16 H), 3.62 (s, 4 H), 7.10 (s, 4 H).

The compound is not very stable. It changed color gradually. The ammonium salt was purified by dissolving in acetonitrile and precipitating with ethyl acetate. This purified ammonium salt changed color very fast in the presence of oxygen and decomposed overnight. The decomposition product is insoluble in water.

B. The dipotassium salt of 1,4-bis(2-nitropropyl)benzene (410 mg, 1.25 mmol) was dissolved in 10 mL of 1-propanol and 10 mL of methanol. Anhydrous tetraethylammonium chloride (0.50 g) was added and the mixture stirred at room temperature for 1 h. Benzene (30 mL) was added and the precipitate was removed by filtration. After removal of the solvent, the residue was purified according to the above precipitation method to give the product

(0.45 g, 70%). The product contained some tetraethylammonium chloride as observed from the NMR spectrum.

C. The following procedure was carried out under argon always. 1,4-Bis(2-nitropropyl)benzene (1.26 g, 5 mmol) was converted to the tetraethylammonium salt by 19.2% Et_4NOH (7.66 g, 10 mmol) in 150 mL of benzene and 50 mL of 98% ethanol. The solution was refluxed and water was removed via a Dean-Stark apparatus. After the calculated amount of water was collected, the solvent was distilled to dryness and the residue cooled. Benzene (20 mL) was added and the product collected by filtration. The product (2.45 g, 96%) was obtained as a light yellow solid. The product is highly hygroscopic and unstable in the presence of oxygen. The ammonium salt is insoluble in HMPA.

1,4-Bis(2-iodo-2-nitropropyl)benzene

1,4-Bis(2-nitropropyl)benzene (1.26 g, 5 mmol) was dissolved in 30 mL of methanol and converted to the tetraethylammonium salt by 20% Et_4NOH (7.66 g, 10 mmol). The solution was added to 20 mL of methanol containing iodine (2.54 g, 10 mmol). The reaction mixture was stirred in the dark for 2 h. The crude product (2.40 g, 95%) was obtained by filtration as a yellow solid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.30 (s, 6 H) 3.62 (d, J = 14 Hz, 2 H) 3.95 (d, J = 14, 1 H) 3.97 (d, J = 14 Hz, 1 H), 7.10 (s, 4 H).

p-Phenylsulfonylbenzyl bromide

The compound was made according to the method of F.J. Lotspeich.[113] After recrystallization from ethanol, the product still contained a little dibrominated product and *p*-phenylsulfonyltoluene as observed from the NMR spectrum. The impure product was used directly without further purification. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.42 (s, 2 H) 7.30-8.10 (m, 9 H).

(*p*-Phenylsulfonyl)benzyldimethylsulfonium bromide

p-Phenylsulfonylbenzyl bromide (5.0 g) was dissolved in 40 mL of diethyl ether and 10 mL of dimethyl sulfide. Some crystals formed after a few minutes. Collection by filtration one week later gave the product (2.20 g, 37%) as white needles: ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.80 (s, 6 H), 4.72 (s, 2 H), 7.30-7.92 (m, 9 H).

(*p*-Phenylsulfonyl)benzyltrimethylammonium bromide

A solution of *p*-phenylsulfonylbenzyl bromide (3.73 g, 12 mmol) and trimethylamine (5 mL, 0.055 mol) in 30 mL of diethyl ether was stirred overnight. The product was collected by filtration and rinsed with benzene. The ammonium salt (3.30 g, 71%) was obtained as a white solid: ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.05 (s, 9 H), 4.52 (s, 2 H), 7.40-8.05 (m, 9 H).

(*p*-Phenylsulfonyl)benzyltriethylammonium bromide

p-Phenylsulfonylbenzyl bromide (3.0 g, 9.6 mmol) was dissolved in 15 mL of triethylamine. The solution was stirred overnight and 50 mL of benzene was then added. The product (1.35 g, 34%) was obtained by filtration. ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.30 (t, J = 7 Hz, 9 H), 3.10 (q, J = 7 Hz, 6 H), 4.40 (s, 2 H), 7.40-8.02 (m, 9 H).

Attempted syntheses of 1-(*p*-phenylsulfonyl)phenyl-2-methyl-2-nitropropane

A. From *p*-phenylsulfonylbenzyl bromide: Under argon, a solution of the sulfone (0.50 g, 1.6 mmol) and the lithium salt of 2-nitropropane (0.30 g, 3.2 mmol) in 10 mL of DMSO was stirred overnight. The reaction was worked up by pouring into 50 mL of water and extracting with ethyl acetate. After removal of the solvent, little residue was obtained. No substitution product was observed as determined from the NMR spectrum.

B. From (*p*-phenylsulfonyl)benzyltrimethylammonium bromide: Under argon, the ammonium salt (1.0 g, 2.7 mmol) was added to 20 mL of DMSO containing the lithium salt of 2-nitropropane (0.60 g, 6.3 mmol). The reaction was stirred overnight and worked up in the usual way, but no identifiable product was isolated.

(*p*-Phenylsulfonyl)benzyltriethylammonium bromide was also used for the above reaction, but still no identifiable product was obtained.

C. From (*p*-phenylsulfonyl)benzyldimethylsulfonium bromide: Under argon, a solution of the sulfonium salt (0.75 g, 2 mmol) and the lithium salt of 2-nitropropane (0.40 g, 4.2 mmol) in 10 mL of DMSO was stirred overnight. Some precipitate formed during the reaction. The product was isolated by pouring into 50 mL of water. The precipitate was collected, but it is insoluble in any solvent. No attempts were made to identify the product.

4,4'-Bis(chloromethyl)diphenyl sulfone

The synthesis of 4,4'-bis(chloromethyl)diphenyl sulfide is based on the procedure for the chloromethylation of methyl phenyl sulfide.[114] $AlCl_3$ (31 g) and dimethoxymethane (9.1 g) were added to the solution of diphenyl sulfide (8.5 mL, 0.05 mol) in 100 mL of dichloroethane. The reaction mixture was stirred for 2 h. and worked up by pouring into 200 mL of water. The dichloroethane layer was separated and dried. After removal of the solvent, the crude product (11.0 g) was obtained. Recrystallization from acetic acid gave the sulfide (5.2 g, 37%) as a light yellow solid: mp 94-95^0 C (lit.[114b] mp 97-98^0 C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.55 (s, 4 H) 7.30 (s, 8 H).

The sulfone was made in 95% yield according to the method of Podkoscielny and Rudz.[115] The crude product was used without further purification. ^{1}H NMR (80 MHz, $CDCl_3$) δ 4.58 (s, 4 H), 7.52 (d, J = 8 Hz, 4 H), 7.93 (d, J = 8 Hz, 4 H).

4,4'-Dichlorodiphenyl sulfone

4,4'-Dichlorodiphenyl sulphoxide was made in 81% yield according to the method of Cumper, Read and Vogel.[116] The crude product was used directly for the next step oxidation. ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.40 (d, J = 8 Hz, 4 H) 7.58 (d, J = 8 Hz, 4 H).

The oxidation procedure employed for 4,4'-bis(chloromethyl)diphenyl sulfide was followed by using 4,4'-dichlorodiphenyl sulfoxide (30.0 g) and 12 mL of hydrogen peroxide and 150 mL of acetic acid. The product was isolated by precipitation with water. Recrystallization of the precipitate from ethanol gave white crystals (30.0 g, 94%): mp 145-146°C (lit.[116] mp 148° C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.45 (d, J = 9 Hz, 4 H), 7.85 (d, J = 9 Hz, 4 H).

4,4'-Bis[(1-hydroxy-1-methyl)ethyl]diphenyl sulfone

Diphenylsulfone-4,4'-dicarboxylic acid was made by oxidation of 4,4'-dimethyldiphenyl sulfone.[87,88] Esterfication of the acid (11.8 g) with ethanol by the Fischer method gave 4,4'-bis(ethoxycarbonyl)diphenyl sulfone (10.9 g, 78%) as a white solid: mp 150-151°C (lit.[87] mp 156-157° C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.40 (t, J = 7 Hz, 6 H) 4.40 (q, J = 7 Hz, 4 H) 7.95-8.13 (m, 8 H).

The Grignard reagent methyl magnesium iodide (40 mmol) was made as usual in diethyl ether. 4,4'-Bis(ethoxycarbonyl)diphenyl sulfone (3.62 g, 10 mmol) was added portionwise. The reaction was refluxed for 2 h. and worked up by pouring into ice-water and extracting with ethyl acetate. After removal of the solvent, the alcohol (2.90 g, 87%) was obtained as a white solid: ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.52 (s, 12 H), 2.10-2.40 (br, 2 H), 7.52-7.90 (m, 8 H). The crude product was used directly for the next reaction step.

4,4'-Bis[(1-chloro-1-methyl)ethyl]diphenyl sulfone

The following method is based on the procedure employed for the preparation of α-chloro-*p*-nitrocumeme.[89] 4,4'-Bis[(1-hydroxy-1-methyl)-ethyl]diphenyl sulfone (3.48 g) was dissolved in 40 mL of dichloromethane. Then zinc chloride (15.0 g, dried under vacuum at 140° C for 24 h. before use) and 30 mL of conc. hydrochloric acid were added to the solution. After stirring for 2 h., the precipitate was removed by filtration. The organic layer in the filtrate was separated and the solvent was evaporated to give the chloride (2.58 g). The precipitate was dissolved in 40 mL of water and extracted with chloroform to give an additional 1.0 g of product; total 3.58 g (93% yield). Attempts to purify the compound by flash chromatography (chloroform as an eluant) were unsuccessful. The product is a white solid: mp 108° C (dec.); ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.95 (s, 12 H), 7.65-8.00 (m, 8 H). Anal. calcd for $C_{18}H_{20}Cl_2O_2S$: C, 58.22; H, 5.43; Cl, 19.10. Found: C, 58.54; H, 5.47; Cl, 17.49.

4,4'-Dinitrodiphenyl sulfone

4,4'-Dinitrodiphenyl sulfide was made in 61% yield according to the method of Price and Stacy;[117] mp 158-159° C (lit.[117] mp 160-161° C).

The sulfide (11.0 g) was dissolved in 200 mL of acetic acid at 80° C. Hydrogen peroxide (20 mL, 30%) was added slowly and the solution was refluxed overnight. The solution was cooled to room temperature and the product (11.2 g, 91%) was collected by filtration. Recrystallization from acetic acid afforded yellow needles: mp 256-258° C (lit.[90] mp 282° C); ^{1}H NMR (80 MHz, DMSO-d_6) δ 8.10-8.50 (m).

4,4'-Dibromodiphenyl sulfone

4,4'-Dibromodiphenyl sulfoxide was made in 66% yield according to the method of Buehler and Masters.[118] The crude product was used for the next reaction. ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.30-7.70 (m).

The sulfoxide was oxidized by using the procedure for the preparation of 4,4'-bis(chloromethyl)diphenyl sulfone. Recrystallization from ethanol-acetic acid gave white crystals: mp 167-168° C (lit.[118] mp 170-171° C); ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.55-7.95 (m).

4,4'-Bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone

A. Attempted synthesis from 4,4'-dibromodiphenyl sulfone: A mixture of the sulfone (0.75 g, 2 mmol) and the lithium salt of 2-nitropropane

(0.40 g, 4.2 mmol) in 10 mL of HMPA was stirred for 24 h. The reaction was worked up by pouring into 50 mL of water. Most of the starting material sulfone was recovered. The reaction was also tried under illumination for 24 h., but still no reaction occured.

4,4'-Dichlorodiphenyl sulfone was used, but no reaction occured. The sulfone was recovered.

B. Attempted synthesis from 4,4'-bis[(1-chloro-1-methyl)ethyl]-diphenyl sulfone: A mixture of the sulfone (0.20 g, 0.54 mmol) and sodium nitrite (0.40 g, 6 mmol) in 10 mL of DMSO was stirred overnight. The reaction was worked up by pouring into 50 mL of water. The starting material was recovered.

C. From 4,4'-dinitrodiphenyl sulfone: Under argon, a solution of the sulfone (0.62 g, 2 mmol) and the lithium salt of 2-nitropropane (0.40 g, 4.2 mmol) in 10 mL of HMPA was stirred for 20 h. The reaction was worked up by pouring into 100 mL of water and the product (0.65 g, 83%) was collected by filtration. Recrystallization from ethanol gave light yellow crystals: mp 200°C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.00 (s, 6 H,) 7.63 (dd, J = 8 and 2 Hz, 2 H), 8.05 (dd, J = 8 and 2 Hz, 2 H). Anal. Calcd for $C_{18}H_{20}N_2O_6S$: C, 55.01; H, 5.14; N, 7.14. Found: C, 54.84; H, 5.21; N, 7.28.

Attempted syntheses of 4,4'-bis[(1,1,2-trimethyl-2-nitro)-propyl]diphenyl sulfone

A. Under argon, a mixture of 4,4'-bis[(1-chloro-1-methyl)ethyl]-diphenyl sulfone (0.37 g, 1 mmol) and the lithium salt of 2-nitropropane (0.40 g, 4.2 mmol) in 10 mL of DMSO was stirred for 24 h. The reaction changed color from yellow to light brown and was worked up by pouring into 50 mL of water. All the starting material sulfone was recovered.

B. A mixture of 4,4'-bis[(1-methyl-1-nitro)ethyl]diphenyl sulfone (0.20 g, 0.5 mmol) and lithium salt of 2-nitropropane (0.20 g, 2.1 mmol) in 10 mL of HMPA was stirred under illumination for 24 h. After workup, all the starting material was recovered.

The lithium salt of methyl 2-cyanobutanoate

Lithium metal (210 mg, 0.030 mol) was converted to lithium methoxide in 30 mL of methanol. Methyl 2-cyanobutanoate (3.91 g, 0.030 mol) was then added to the solution. The solvent was evaporated until precipitate just appeared. The lithium salt (3.60 g, 90%) was obtained by precipitation with diethyl ether as a white solid: ^{1}H NMR (80 MHz, D_2O) δ 1.00 (t, J = 7 Hz, 3 H) , 2.05 (q, J = 7 Hz, 2 H), 3.30 (s, 3 H).

Methyl 2-cyano-2-ethyl-3-methyl-3-nitrobutanoate

A. The lithium salt of 2-nitropropane (0.20 g, 2 mmol) was added to the solution of methyl 2-cyano-2-nitrobutanoate (0.17 g, 1 mmol) in 10 mL of DMSO. The reaction was stirred at room temperature overnight and worked up by pouring into 50 mL of water. The product was extracted with dichloromethane. The combined extracts were dried and evaporated. The crude product (0.20 g, 94%) was obtained as a mixture of diastereoisomers and was purified by dissolving in diethyl ether and cooling in dry ice to give white crystals: mp 50-51°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.13 (t, J = 7 Hz, 3 H), 1.86 (qd, J = 7 and 14 Hz, 1 H), 1.84 (s, 3 H), 1.88 (s, 3 H), 2.16 (qd, J = 7 and 14 Hz, 1 H), 3.86 (s, 3 H). Anal. Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.36; H, 6.56; N, 13.15.

B. Under argon, the lithium salt of methyl 2-cyanobutanoate was added to 10 mL of DMSO containing 2,2-dinitropropane (134 mg, 1 mmol). The reaction was stirred for 24 h. and worked up according to the above procedure. The crude product (0.16 g, 74%) was obtained.

C. Under argon, 2-nitropropane (0.36 g, 4 mmol) was converted to the tetraethylammonium salt by 20% Et_4NOH (2.90 g, 4 mmol) in 10 mL of DMSO. Methyl 2-bromo-2-cyanobutanoate (0.41 g, 2 mmol) was added to the solution. The reaction was illuminated with stirring for 20 min. and worked up by pouring to 50 mL of water. The product was extracted with dichloromethane. After removal of the solvent, the residue (0.35 g) contained the expected product methyl 2-cyano-2-ethyl-3-methyl-3-nitrobutanoate and

2,3-dimethyl-2,3-dinitrobutane in a ratio of approximately 3:1 as determined from the NMR spectrum.

Dimethyl 2,3-dicyano-2,3-diethylsuccinate

A. Attempted synthesis from methyl 2-cyano-2-nitrobutanoate: Under argon, methyl 2-cyano-2-nitrobutanoate (0.17 g, 1 mmol) and the lithium salt of methyl 2-cyanobutanoate (0.30 g, 2.3 mmol) were dissolved in 5 mL of HMPA. The reaction was illuminated with stirring for 5 h., and worked up in the usual way. No identifiable product was isolated.

B. Under argon, methyl 2-cyanobutanoate (0.25 g, 2 mmol) was converted to the tetraethylammonium salt by 20% Et_4NOH (1.47 g, 2 mmol) in 10 mL of HMPA. Methyl 2-bromo-2-cyanobutanoate (0.21 g, 1 mmol) was added to the solution. The reaction was illuminated with stirring for 2 h. and worked up by pouring into 50 mL of water. The product was collected by filtration. It is a mixture of *dl* and *meso* isomers. Recrystallization from methanol gave the dimer (0.17 g, 68%) as white crystals: mp 130-136°C; ^1H NMR (200 MHz, $CDCl_3$) δ 1.12 (t, J = 7 Hz, 3 H), 1.19 (t, J = 7 Hz, 3 H), 1.88-2.20 (m, 2 H), 2.22-2.48 (m, 2 H), 3.86 (s, 3 H), 3.90 (s, 3 H). Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10. Found: C, 56.83; H, 6.23; N, 11.09.

C. Under argon, methyl 2-cyanobutanoate (1.52 g, 0.012 mol) was converted to the tetraethylammonium salt by 20% Et_4NOH (8.82 g, 0.012 mol) in 15 mL of DMSO. Iodine (1.02 g, 4 mmol) was added to the solution.

The reaction was illuminated with stirring for 7 h., and worked up in the usual way to give the product (0.61 g, 61%).

3. Polymerization

Polymerization of the dilithium salt of 1,4-bis(2-nitropropyl)benzene with 1,4-bis(2,2-dinitropropyl)benzene

Gerneral procedure: Under argon, the dilithium salt of 1,4-bis(2-nitropropyl)benzene (0.264 g, 1 mmol) and 1,4-bis(2,2-dinitropropyl)benzene (0.342 g, 1 mmol) were mixed in 30 mL of HMPA. During the reaction the dilithium salt dissolved slowly. After being stirred with or without illumination for a certain time, the reaction was worked up by pouring into 120 mL of water. The yellow precipitate was collected and dried by air. The yield was measured according to the weight.

The product was purified by dissolving in 20 mL of chloroform and precipitating with 100 mL of methanol. This precipitate was collected by filtration. After the polymer was dried, the molecular weight was measured by osmometric method (acetone or benzene as solvents). The molecular weight of product obtained from different reaction conditions is summarized in Table IV. The polymer is a light yellow solid: mp 90-100° C; FT-IR ($CHCl_3$ cast) 1550 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.1-1.5 (br), 1.54 (d, J = 7 Hz), 1.60-2.20 (br), 2.8-3.3 (br), 3.0 (q, J = 7 Hz), 3.3 (q, J = 7 Hz), 3.5-3.9 (br), 4.0-4.5 (br), 4.75 (m, J = 7 Hz), 6.7-7.5 (br). The integration ratio of the signals at δ 4.0-4.5 and 4.75 ppm is about 4:1.

Table IV. Molecular weights of products obtained from different reaction conditions.

Light Source	Time (day)	Yield (%)	Molecular weight
lab light	1	100	574[a]
lab light	7	100	751[b]
lab light	30	92	843[b]
fluoroscent light	2	96	834[b]

[a] Benzene was used as a solvent for the molecular weight analysis.
[b] Acetone was used as a solvent for the molecular weight analysis.

Determination of the concentration of Et_4NOH

The labelled concentration of commercially available product Et_4NOH is 20% by weight. The concentration was determined to be 19.2% by weight by titration with 1 N HCl (phenolphthalein as an indicator).

The concentration was also measured by the reaction of 2-nitro-1-phenylpropane with iodine in the presence of various amounts of Et_4NOH. The following general procedure was used. Under argon, 2-nitro-1-phenylpropane (2 mmol) was converted to the ammonium salt by Et_4NOH in 15 mL of solvent. Iodine (254 mg, 1 mmol) was then added. The reaction mixture was stirred under illumination for 20 min. and worked up by pouring into 100 mL of water. The precipitate was collected. After being dried by air, the yield was measured according to the weight. Table V summarizes the reaction of 2-nitro-1-phenylpropane with iodine in the presence of various amounts of Et_4NOH.

Table V. Estimation of the concentration of Et_4NOH determined by the reaction of 2-nitro-1-phenylpropane with iodine in various amounts of Et_4NOH.

solvent	Et_4NOH (g)	yield (%)	calculated concentration (%)*
CH_3CN	1.60	94	18.4
HMPA	1.53	79	19.2
DMSO	1.63	85	18.0
DMSO	1.68	82	17.5

*The concentration c of Et_4NOH is calculated by the following equation :

$$c = 2 \times 10^{-3} \times 147/w$$

2×10^{-3} is the molarity of 2-nitro-1-phenylpropane (2 mmol) used for the coupling reaction. 147 is the molecular weight (g/mol) of Et_4NOH. w is the weight (g) of Et_4NOH used for the reaction.

Polymerization by the reaction of the di-tetraethylammonium salt of 1,4-bis(2-nitropropyl)benzene with iodine

A. 1,4-Bis(2-nitropropyl)benzene (0.63 g, 2.5 mmol) was converted to the tetraethylammonium salt in 20 mL of DMSO by 18.4% Et_4NOH (3.99 g, 5 mmol). Iodine (0.64 g, 2.5 mmol) was added to the resulting yellow solution. The reaction was illuminated with a fluorescent light for 24 h. and worked up by pouring into 100 mL of water. The precipitate was collected and dried. The polymer is a light yellow solid. It is only slightly soluble in HMPA at room temperature and slightly soluble in DMSO at 100° C.

The crude product was mixed with 15 mL of HMPA containing $Na_2S{\cdot}10H_2O$ (2.0 g). The mixture was stirred and illuminated for 24 h. The product was isolated by pouring into 100 mL of water (several drops of acetic acid may be added if a colloidal solution forms). Collection of the precipitate gave the elimination polymer as a light yellow solid (0.56 g). This polymer was purified by dissolving in 20 mL of chloroform and precipitating with methanol. The precipitate was collected and dried. The purified sample contained sulfur (S_8) as indicated from the mass spectrum. After being dried at 80° C under vacuum overnight, the polymer became an insoluble material.

B. 1,4-Bis(2-nitropropyl)benzene (0.63 g, 2.5 mmol) was converted to the tetraethylammonium salt in 20 mL of DMSO using the above method. Iodine (335, 202 and 72 mg) was added portionwise in every 20 min. After being stirred for 24 h. under illumination, the reaction was worked up according to the above procedure. The crude product was also reduced by

$Na_2S{\cdot}10H_2O$ (2.0 g) in 15 mL of HMPA. After workup, the crude elimination product (0.56 g) was obtained. The polymer also contained sulfur as indicated from the mass spectrum. After being heated at 80° C under vacuum overnight, the polymer became an insoluble material.

C. The polymerizaton using the method A was repeated in DMSO. The crude product (0.56 g) was obtained by precipitation with water. After being dried by air, the crude product reacted with the lithium salt of 2-nitropropane (1.5 g) in 15 mL of HMPA under illumination under argon. The solid dissolved in 7 days. The elimination polymer was isolated by precipitation with water. The crude product (0.48 g) was obtained as a yellow solid. It is a mixture of the elimination polymer and 2,3-dimethyl-2,3-dinitrobutane as indicated from the NMR spectrum. 2,3-Dimethyl-2,3-dinitrobutane was removed by extraction with boiling methanol (3 × 20 mL). The polymer (0.12 g) was obtained after the extraction. It is a light yellow solid and decomposes at 230° C. It is soluble in $CHCl_3$, CH_2Br_2 and pyridine, but insoluble in benzene and acetone. The sample was further purified by mixing with 5 mL of ethyl acetate. The solvent was decanted after being stood overnight. The precipitate was collected and dried. ^1H NMR (200 MHz, $CDCl_3$) δ 1.68 (s, 3 H), 1.74 (s, 3 H), 3.26 (s, 2 H), 3.32 (s, 2 H), 7.16 (s, 4 H). FT-IR ($CHCl_3$ cast) 1547, 1508 cm^{-1}. MS (FAB) the following peaks above 1000 (intensity) were observed: 1429 (0.06), 1427 (0.06), 1346 (0.07), 1218 (0.11), 1128 (0.08), 1044 (0.08), 1041 (0.03). Anal. Calcd for $C_{12}H_{14}$ (Polymer structure in equation 95): C, 91.08; H, 8.92. Found: C, 77.56; H, 7.75; N, 3.84.

Determination of molecular weight of the elimination polymer by osomometric method

A. in pyridine: The polymer is soluble in pyridine to form a yellow solution. However, during the molecular weight analysis in the osomometer, the osomotic pressure increases in the beginning and then dropped gradually. It could not give a stable reading. Thus an alternative solvent was used for the molecular weight analysis.

B. in dibromomethane: The polymer is soluble in dibromomethane to form a colorless solution. The average molecular weight is 4888.

4. Franchimont Reaction

Methyl 2-cyanobutanoate

A. Methyl 2-bromobutanoate (0.45 g, 2.5 mmol) was added to 10 mL of DMSO containing glacial acetic acid (0.30 g, 5 mmol) and sodium cyanide (0.49 g, 10 mmol). After being stirred for 4 h, the reaction was worked up by pouring into 50 mL of water and acidifying with 1 N HCl. The product was extracted with 3 × 20 mL of dichloromethane. The combined extracts were rinsed with water and dried ($MgSO_4$). The product (0.21 g, 66%) was obtained after removal of the solvent. It was quite pure as determined by the NMR spectrum.

B. Methyl 2-bromobutanoate (0.91 g, 5 mmol) was added to 10 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (1.90 g, 10 mmol), triethylamine (1.52 g, 15 mmol) and sodium cyanide (0.49 g, 10 mmol). The reaction was stirred for 12 h. and worked up in the usual way. Removal of the solvent gave the product (0.48 g, 75%) whose NMR spectrum was that of the pure compound.

C. Acetic acid (2.40 g, 0.040 mol) and sodium cyanide (3.92 g, 0.080 mol) were added to 30 mL of methanol containing methyl 2-bromobutanoate (1.80 g, 0.010 mol). The reaction was stirred for 18 h. and worked up in the usual way. The reaction was only 60% complete as determined from the NMR spectrum. Even after 52 h., the reaction was still only 80% complete.

D. Methyl 2-bromobutanoate (0.91 g, 5 mmol) was added to a mixture of 10 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (2.85 g, 15 mmol), dimethylbenzylamine (3.40 g, 25 mmol) and sodium cyanide (0.75 g, 15 mmol). The reaction was stirred for 24 h. and worked up in the usual way to give the crude product (0.60 g). The reaction was only 84% complete.

E. Methyl 2-bromobutanoate (0.91 g, 5 mmol) was added to 20 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (2.85 g, 15 mmol) and sodium cyanide (0.74g, 15 mmol). The reaction was stirred for 24 h. and worked up in the usual way. The starting material was recovered.

F. Methyl 2-bromobutanoate (0.91 g, 5 mmol) was added to 20 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (1.90 g, 10 mmol), N,N-dimethylaniline (1.21 g, 10 mmol) and sodium cyanide (0.49 g, 10 mmol). The reaction was stirred at 50° C for 24 h. Only starting material was recovered.

When acetic acid was used instead of *p*-toluenesulfonic acid, a mixture of methyl 2-cyanobutanoate (60%) and 2-acetoxybutanoate (40%) was obtained as determined from the NMR spectrum.

G. Acetic acid (1.5 mL, 25 mmol) and sodium cyanide (0.74 g, 15 mmol) were added to 10 mL of DMSO containing methyl 2-bromobutanoate (0.91 g, 5 mmol). The reaction was stirred overnight and worked up in the usual way. Two products methyl 2-cyanobutanoate and methyl 2-acetoxybutanoate in 1:1 ratio were obtained as determined from the NMR spectrum. No attempt was made to separate the mixture. ^{1}H NMR (80 MHz,

$CDCl_3$) for methyl 2-acetoxybutanoate δ 4.98 (t, J = 6 Hz, 1 H), 3.78 (s, 3 H), 2.15 (s, 3 H), 1.00 (t, J = 7 Hz, 3 H). The signal of the methylene protons is overlapped with that of methyl 2-cyanobutanoate.

Methyl α-bromophenylacetate

Phenylacetic acid (8.2 g, 0.060 mol) was refluxed with thionyl chloride (10 mL) for 4 h. The excess thionyl chloride was removed by distillation. Bromine (3.4 mL, 0.066 mol) was then added and the reaction was warmed to 70°C overnight. The acetyl chloride was esterified by addition of methanol (10 mL) and then poured into 100 mL of water. Extraction with dichloromethane and evaporation of the solvent left the residue, which was distilled to give the product (11.5 g, 84%) as a liquid: bp 72-74°C (0.5 mm) [lit.[120] 172°C (53 mm)]; ^1H NMR (80 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 5.33 (s, 1 H), 7.20-7.62 (m, 5 H).

Methyl α-cyanophenylacetate

A. Sodium cyanide (0.49 g, 0.010 mol) was added to 10 mL of DMSO containing methyl α-bromophenylacetate (1.15 g, 5 mmol). The reaction was stirred for 3 hours and worked up in the usual way. The product contained the cyanoester (30%) and the dimer dimethyl 2-cyano-2,3-diphenylsuccinate (70%) as estimated from the NMR spectrum.

B. Methyl α-bromophenylacetate (1.15 g,5 mmol) was mixed with 20 mL of DMSO containing acetic acid (1.20 g, 0.020 mol) and sodium cyanide (1.5 g, 0.030 mol). The reaction mixture was stirred overnight and worked up in the usual way to give a mixture of dimethyl 2-cyano-2,3-diphenylsuccinate and methyl α-acetoxyphenylacetate (in about 1:3 ratio) as determined from the NMR spectrum.

C. Acetic acid (1.20 g, 0.020 mol) and sodium cyanide (0.49 g, 0.010 mol) were added to 20 mL of DMSO containing methyl α-bromophenylacetate (1.20 g, 5 mmol). The reaction was stirred overnight and worked up in the usual way. Only methyl α-acetoxyphenylacetate was obtained as observed from the NMR spectrum. No attempts were made to purify the product and measure the yield. ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.18 (s, 3 H), 3.70 (s, 3 H,) 5.93 (s, 1 H), 7.25-7.26 (m, 5 H).

D. Methyl α-bromophenylacetate (1.15 g, 5 mmol) was added to 20 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (1.90 g, 10 mmol) and sodium cyanide (0.49 g, 10 mmol). The reaction was stirred for 24 h. and worked up in the usual way. The product contained 40% methyl α-bromophenylacetate and 60% methyl α-hydroxyphenylacetate as estimated from the NMR spectrum. After stirring for 4 days, only methyl α-hydroxyphenylacetate was obtained. ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.58 (d, J = 6 Hz, 1 H) 3.70 (s, 3 H) 5.15 (d, J = 6 Hz, 1 H) 7.33 (s, 5 H). After D_2O exchange, the peak at δ 3.58 ppm disappears and the peak at δ 5.15 ppm changes to a singlet. The chemical shift is identical to that in the literature.[121]

E. Methyl α-bromophenylacetate (1.15 g, 5 mmol) was added to 30 mL of DMSO containing N,N-dimethylaniline (2.42 g, 20 mmol), *p*-toluenesulfonic acid monohydrate (3.80 g, 20 mmol) and sodium cyanide (0.74 g, 15 mmol). The reaction was stirred for 18 h. and worked up in the usual way. A mixture of 45% starting material methyl α-bromophenylacetate, 40% methyl α-hydroxyphenylacetate and 15% methyl α-cyanophenylacetate was obtained as estimated from the NMR spectrum.

F. Methyl α-bromophenylacetate (0.57 g, 2.5 mmol) in 10 mL of DMSO was dropped to 5 mL of DMSO containing tetraethylammonium cyanide[123] (1.95 g, 12.5 mmol). The reaction was stirred for 1 h. and worked up in the usual way. The crude product methyl α-cyanophenylacetate (0.44 g, 100%) was obtained as a liquid: ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.75 (s, 3 H), 4.70 (s, 1 H), 7.35 (s, 5 H). The chemical shift is identical to that in the literature.[122]

Attempted syntheses of diethyl 2,5-dicyanoadipate

A. Sodium cyanide (2.0 g, 0.41 mol) was added to 20 mL of DMSO containing diethyl 2,5-dibromoadipate[124] (3.36 g, 9.3 mmol). The reaction was stirred for 24 h. and worked up in the usual way. After distillation, a mixture of *trans* and *cis* diethyl 1-cyanocyclobutane-1,2-dicarboxylate (1.62 g, 72%) was obtained as a liquid: bp 104-106°C (0.5 mm) [lit.[92a] 152-154°C (9 mm)]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10-1.25 (m, 6 H), 2.25-2.75 (m, 4 H), 3.65-3.95 (m, 1 H), 4.05-4.50 (m, 4 H).

B. The reaction of diethyl 2,5-dibromoadipate with NaCN in 40% DMSO at 80°C was reported to give diethyl 2,5-dicyanoadipate.[96] The reaction was repeated three times, but only the cyclized product was obtained.

Attempted syntheses of dimethyl 2,5-dicyanoadipate

A. Sodium cyanide (3.0 g, 0.061 mol) was added to 30 mL of DMSO containing dimethyl 2,5-dibromoadipate [93b] (5.0 g, 15 mmol). The mixture was stirred for 24 h. and worked up by pouring into 100 mL of water and acidifying with 1 N HCl. The product was extracted with 3 × 30 mL of benzene. After removal of the solvent, the residue was distilled to give a mixture of *cis* and *trans* dimethyl 1-cyanocyclobutane-1,2-dicarboxylate (2.20 g, 73%) bp 90-96°C (0.5 mm) [lit.[93b] bp 119-120°C (2 mm)]. One of the isomers crystallized in the distillate. The crystals were collected and recrystallized from methanol, mp 87-88°C [lit.[93b] mp 89.5-90°C]. ^{1}H NMR (200 MHz, $CDCl_3$) for the solid isomer δ 2.30-2.46 (m, 1 H), 2.56-2.84 (m, 3 H), 3.72 (s, 3 H), 3.85 (s, 3 H), 3.74-3.84 (m, 1 H); For the liquid isomer δ 2.26-2.38 (m, 1 H), 2.52-2.72 (m, 3 H), 3.80 (s, 3 H), 3.89 (s, 3 H), 3.82-3.86 (m, 1 H).

B. Dimethyl 2,5-dibromoadipate (3.32 g, 0.010 mol) was added to 20 mL of DMSO containing acetic acid (2.0 mL, 0.033 mol) and sodium cyanide (4.4 g, 0.09 mol). The reaction was stirred for 24 h. and worked up in the usual way. After distillation, the cyclized product (1.46 g, 65%), dimethyl 1-cyanocyclobutane-1,2-dicarboxylate, was obtained.

C. Acetic acid (3.6 mL, 0.060 mol) and sodium cyanide (4.90 g, 0.010 mol) were added to 30 mL of methanol containing dimethyl 2,5-dibromoadipate (0.50 g, 1.5 mmol). The reaction was stirred overnight and worked up in the usual way. Only the cyclized product was obtained. No attempts were made to measure the yield.

D. Dimethyl 2,5-dibromoadipate (1.0 g, 3 mmol) was added to 20 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (2.30 g, 12 mmol), N,N-dimethylaniline (1.45 g, 12 mmol) and sodium cyanide (0.59 g, 12 mmol). The reaction was stirred for 4 days and worked up in the usual way. The starting material dimethyl 2,5-dibromoadipate was recovered.

When the above reaction was attempted using triethylamine (1.21 g, 12 mmol), only the cyclized product dimethyl 1-cyanocyclobutane-1,2-dicarboxylate was obtained.

E. Tetraethylammonium cyanide (1.5 g, 0.010 mol) was dissolved in 15 mL of DMSO. Acetic acid (0.12 g, 2 mmol) and dimethyl 2,5-dibromoadipate (0.33 g, 1 mmol) were added to the solution. The reaction was stirred for 20 min. and worked up in the usual way. Only the cyclized product was observed from the NMR spectrum.

F. Dimethyl 2,5-dibromoadipate (0.66 g, 2 mmol) in 10 mL of DMF was dropped into the mixture of tetraethylammonium cyanide (3.1 g, 0.020 mol) in 20 mL of DMF cooled to -30°C. The reaction was stirred at -30°C for 10 h. and 2 mL of acetic acid was added. The reaction was worked up in the usual way. Only the cyclized product was obtained.

The above reaction was tried by using acetic acid (0.60 g, 10 mmol) as a buffer. Besides the cyclobutane, an unknown compound was obtained. ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.95-5.12 (m, 1 H), 3.76 (s, 3 H), 3.77 (s, 3 H), 2.14 (s, 3 H), 2.15 (s, 3 H). It is probably dimethyl 2,5-diacetoxyadipate. No attempts were made to separate and idetnify the unknown compound.

2-Cyano-2-methoxycarbonylcyclobutanecarboxylic acid

A. Tetraethylammonium cyanide (2.1 g, 32 mmol) was dissolved in 10 mL of DMSO at 50° C. Dimethyl 2,5-dibromoadipate (0.66 g, 2 mmol) was added to the solution. The reaction was stirred overnight at 50° C, and worked up by pouring into 50 mL of water and acidifying with 1 N HCl. The product was extracted with ethyl acetate. The combined extracts were dried and evaporated. The residue, obtained after evaporation of the solvent, was a deep brown oil. The product is probably *trans* and *cis*-2-cyano-2-methoxycarbonylcyclobutane-carboxylic acid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.28-2.42 (m, 2 H), 2.58-2.78 (m, 6 H), 3.75 (s, 3 H), 3.83 (s, 3 H), 3.74-3.90 (m, 2 H), 7.06-7.24 (b, 2 H). FT-IR ($CHCl_3$ cast) 2700-3400 (broad), 1731 cm^{-1}.

B. The above reaction was tried using tetraethylammonium cyanide (1.25 g, 16 mmol). A mixture was obtained when the reaction was stirred at 50° C for 20 h. The signals for the methyl groups were located at δ 3.73, 3.75, 3.80, 3.83, 3.86, 3.89 ppm respectively.

C. Tetraethylammonium cyanide (1.50 g, 9.6 mmol) was dissolved in 5 mL off DMSO containing *p*-toluenesulfonic acid monohydrate (0.20 g, 1 mmol). Dimethyl 2,5-dibromoadipate (0.50 g, 1.5 mmol) was added. The reaction was stirred at 50° C for 5 min. and worked up in the usual way. The mixture also showed six singlets for the methyl protons at δ 3.73, 3.75, 3.80, 3.83, 3.86 and 3.89 ppm.

2-Cyano-2-methoxycarbonylcyclohexanecarboxylic acid

Tetraethylammonium cyanide (6.2 g, 0.040 mol) was dissolved in 20 mL of DMSO containing *p*-toluenesulfonic acid monohydrate (0.80 g, 4 mmol). The solution was warmed to 50° C. Dimethyl 2,7-dibromosuberate[125] (1.44 g, 4 mmol) was then added. The reaction was stirred at this temperature overnight and worked up by pouring into 100 mL of water. After acidification with 1 N HCl, the product was extracted with chloroform. The combined extracts were washed with water and dried. Removal of the solvent gave a residue, which was recrystallized from benzene to give a white solid (0.40 g, 48%): mp 140-142° C (dec.); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26-2.00 (m, 6 H), 2.22-2.40 (m, 2 H), 2.98 (dd, J = 4, 13 Hz, 1 H), 3.76 (s, 3 H), 7.08 (br, 2 H) (the broad peak at 7.08 ppm is exchangeable with D_2O); FT-IR ($CHCl_3$ cast) 3200-2800, 2240, 1733, 1713, 1211 cm^{-1}; ^{13}C NMR ($CDCl_3$) 173.88, 172.03, 117.19, 52.65, 48.05, 47.30, 34.65, 25.30, 24.65, 21.81; CIMS (ammonia), *m/z* 229 (M^+ + 18, base). Anal. Calcd for

$C_{10}H_{13}NO_4{\cdot}(H_2O)_{1/2}$: C, 54.54; H, 6.41; N, 6.36. Found: C, 54.79; H, 6.36; N, 6.30.

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